

INDUSTRIAL CHEMICAL CALCULATIONS

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THE APPLICATION OF
PHYSICO-CHEMICAL PRINCIPLES AND DATA
TO PROBLEMS OF INDUSTRY

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PREFACE TO THE SECOND EDITION

During the five years following the first edition of this book the chemical engineering profession has progressed rapidly in the development of quantitative and exact methods of treating its problems. At the same time the problems have become more complex with the increasing application of high temperature and pressure processes.

These developments have strengthened the opinion that there is need for more thorough training of chemical engineers in the exact and quantitative application of fundamental physicochemical principles to industrial problems as covered in this book.

In the second edition extensive changes have been made in order to keep pace with the developments of the field. The thermodynamic approach to problems involving non-ideal conditions has been advanced to practical utility through the development of generalized relationships to fill the gaps of missing data until it has become essential that a well-trained chemical engineer be familiar with these methods. This has led to the introduction in this book of the concepts of entropy, free energy, fugacity, and activity, and their applications to industrial problems. The rather cumbersome kinetic-theory approach to the principles of equilibrium has been discarded in favor of the more concise and exact thermodynamic methods.

The introduction of thermodynamic methods made desirable a complete reorganization of the text. The first nine chapters, designated as Part I, are now limited to treatment of ideal, low-pressure systems in which simple algebraic methods can be used. Chapters IX to XIV treat non-ideal cases by more general and complicated methods, involving considerable use of the calculus.

The entire arrangement has been made one of progressively increasing complexity, which it is believed will make this edition much more understandable and teachable than the first, in which non-ideal deviations were introduced concurrent with the simple ideal principles.

Chapter XII of the first edition dealing with distillation equilibria has been omitted because this material in part belongs more properly to a course in the unit operation of chemical engineering under distillation. The newer developments of vaporization equilibria at higher pressures involving the use of the vaporization equilibrium constant expressed in terms of fugacities are not sufficiently developed to warrant textbook presentation.

Throughout the entire book emphasis has been placed on generalized methods of predicting the missing physicochemical data that hamper almost every industrial problem. In Chapter VII new methods are presented for estimating the combustion properties of petroleum fuels. In Chapters XI and XIII are new generalized methods for estimating compressibility factors, fugacities, enthalpies, and heat capacities in the absence of specific data.

Chapter VIII dealing with heat and weight balances of combustion processes has been reorganized, consistent with the general arrangement of the text, to start with the most simple cases and from them develop the more complex.

In Chapter X the calculations of crystallization have been developed by much more concise methods, and for the treatment of the accompanying thermal changes the enthalpy-concentration charts have been introduced.

In the first chapter a section devoted to the conversion of units has been added. The use of the weight balance and the heat balance has been given more emphasis throughout the early chapters than in the first edition.

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PREFACE TO THE FIRST EDITION

In the following pages certain industrially important principles of chemistry and physics have been selected for detailed study. The significance of each principle is extensively developed and its applicability and limitations scrutinized. Direct and logical methods of calculation are then presented illustrating the use and combination of these principles in solving typical industrial problems.

There is no intent that the study of the contents of this book should in any way replace a general course in physical chemistry. Furthermore, no attempt has been made to discuss the unit operations of chemical engineering or the more specialized and advanced studies of chemical engineering operations and design. A study of this book will rather serve to supplement a course in physical chemistry and to give better preparation for advanced courses in chemical engineering.

It is well recognized that the general college course in elementary physics can be expected to give only a superficial survey of a very broad field. For this reason, in the training of structural and electrical engineers, such courses have long been supplemented by intensive courses in applied physics, such as mechanics and electrical principles, to prepare the student adequately for the more advanced courses in the design of structures or electrical equipment. This book has been written primarily to fill a similar need which it is felt exists in the training of chemical and metallurgical engineers. General courses in physics and physical chemistry cannot give the average student the thorough familiarity with the practical applications of fundamental principles which is necessary in the analysis and solution of complicated industrial problems. In such general courses consideration is limited to simple, ideal cases, and little training is offered in developing the analytical, quantitative type of reasoning which is essential if complicated industrial problems are to be solved.

It is considered necessary that in a book of this type the presentation of each subject should be complete, starting with the most elementary concepts, to insure thorough understanding of fundamental principles and to discourage superficial memorizing. This treatment results in a duplication of some of the more fundamental material which is contained in every book on general physical chemistry. However, this is by no means intended as a general textbook on physical chemistry and could

in no sense be used as such. The subjects which are treated here constitute only a very small fraction of those discussed in even the most elementary physical chemistry textbook. No attention is given to experimental methods and apparatus or to many of the most interesting of modern physicochemical topics such as atomic structure, radiation, colloidal behavior, electrochemistry, chemical thermodynamics, photochemistry, and the like.

On the other hand, no general textbook on physical chemistry can adequately cover the material presented herein. With only a few exceptions, each subject is more intensively developed from a theoretical standpoint than in even advanced treatises on physical chemistry. However, all such theoretical discussions are but incidental to the main objective of the book, namely, the development of concise and logical methods by which complex industrial chemical problems may be solved from fundamental scientific principles.

Considerable attention has been devoted to the kinetic theory of matter, in spite of its well-recognized limitations. It has been found that clear-cut kinetic pictures of the mechanisms of gaseous behavior, vaporization, equilibria, and the like are of great value in developing the intelligent use of the mathematical relationships applicable to these problems.

It is believed that the material herein presented will prove valuable to the industrial chemist and also to industrial engineers who are not trained primarily in the chemical field. For the industrial chemist this book offers training in quantitative reasoning and in methods of calculation, and leads to a familiarity with the technical terms and units of industry. For the industrial engineer there is offered a concise presentation of many of the most important principles of physical chemistry, training in the solution of problems by scientific rather than by empirical methods, and an introduction to sources of important engineering data which are otherwise concealed under a guise of unfamiliar terms.

The application and combination of principles are illustrated by detailed solutions of typical problems. These illustrations are selected to represent, wherever possible, actual conditions which might reasonably be met with in industrial practice. In the calculations which are presented, care is taken that the reasoning is logical and apparent. Each individual step is indicated and completely labeled. Arithmetical short-cuts and condensed forms of calculation are avoided in order to clarify the reasoning. Shorthand methods for the indication of calculations result in the saving of time only for the calculator who is experienced and proficient. In industrial practice it is necessary not only to obtain a solution rapidly but also to present this solution in such form that its correctness is certain. The additional time spent in placing

calculations in a clear, well-labeled form is more than regained in the saving of time necessary for positive verification.

Proficiency in analyzing and solving problems can be attained only through actual practice. At the end of each chapter, problems are presented to be solved by the reader. Wherever possible, these problems are selected to represent actual conditions of industrial practice in order that the data may be educational in themselves.

It has been attempted to present principles in such a manner that the only knowledge which is prerequisite for the reader will be that obtained in the general courses of college chemistry and physics. In the presentation of this material in the authors' courses it has been found that engineering students who have not studied physical chemistry have no particular difficulty in grasping the new principles which are involved. However, it is believed that study of this book is most advantageously supplemented by a general course in physical chemistry.

Inclusion of extensive tables of data is beyond the scope of a general text. However, many condensed tables and charts are incorporated to supply data for the problems and illustrations and to serve for convenient reference. Such data are taken from the most modern and authentic sources and are presented in forms and units which are convenient for industrial use.

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INDUSTRIAL CHEMICAL CALCULATIONS

PART I

CHAPTER I

WEIGHTS AND COMPOSITIONS

The principal objective to be gained in the study of this book is the ability to reason accurately and concisely in the application of the elementary principles of physics and chemistry to the solution of industrial problems. It is necessary that each fundamental principle be thoroughly understood, not superficially memorized. However, even though a knowledge of elementary scientific principles is possessed, special training is required to solve the more complex industrial problems. There is a vast difference between the mere possession of tools and the ability to handle them skilfully. Unless especially trained in straightforward, orderly methods of solving quantitative problems which involve scientific principles, students will usually attack such problems in a cumbersome, roundabout fashion.

Direct and logical methods for the combination and application of certain principles of chemistry and physics are described in the text and indicated by the solution of illustrative problems. These illustrations should be carefully studied and each individual operation justified. However, it is not intended that these illustrations should serve as forms for the solution of other problems by mere substitution of data. Their function is to indicate the organized type of reasoning which will lead to most direct and clear solutions. In order to test the understanding of principles and to develop the ability of organized, analytical reasoning, practice in the actual solution of typical problems is indispensable. The problems selected represent, wherever possible, reasonable conditions of actual industrial practice.

Composition Changes. Many processes of industrial importance are of the type which produces, as its ultimate effect, merely a change in the composition of a mixture or solution due to the addition or removal of one or more components. For example, in evaporation the composition of a solution is changed by removal of the solvent. In drying processes the composition of a mixture is changed by the removal of a liquid. The

WEIGHTS AND COMPOSITIONS

composition of a solution is changed in crystallization by removal of solute, and in the reverse process of dissolution by the addition of solute. In the processes of leaching, extraction, and gas-absorption the compositions of mixtures are changed by the removal of certain soluble materials. Such changes in composition are produced in many materials by the natural, uninduced progress of these processes incidental to conditions of storage or treatment. A majority of industrial products readily undergo changes in moisture content under the normal conditions of storage.

Classification of Problems. When materials are added to or removed from a mixture or solution it is frequently of interest to determine the relationship between the initial and final weights and compositions of the mixture or solution and the weight and composition of the material added or removed. If all these quantities may be directly measured no calculation is necessary. However, in general it is not necessary or desirable to make such complete measurements, and problems arise in which one wishes to calculate the required information on the basis of a minimum number of direct measurements. In manufacturing operations there is always a great economic advantage in saving of time and labor if desired information can be obtained by simple calculations with the least number of actual measurements. These problems may be classified in three groups:

1. The initial composition and weight of a mixture or solution are known and it is required to calculate its weight and composition after the addition or removal of a specified weight of material of known composition.

2. The initial composition of a mixture or solution is known together with its composition after the removal or addition of some components. The weight of either the initial or final material is known. It is required to calculate the composition and weight of the material which was added or removed.

3. The initial composition of a mixture or solution is known together with its composition after the removal or addition of some components. The weight and composition of the material added or removed are known. It is required to calculate the weights of the original and final mixtures.

Methods of Solution. Problems of the first type may be readily solved by selecting as the basis of the calculation a definite, specified quantity of the original mixture. The weight of each component present in this basic quantity is determined by the composition. The weight of each component present in the quantity of material which is added to or subtracted from the original mixture is then calculated. By adding to the weight of each component originally present the weight of that

After standing in the yards for some time it is found that the composition of the coal has changed, owing to loss of moisture. The final composition is:

Moisture.....	4.0%
Volatile matter.....	38.7%
Fixed carbon.....	51.0%
Ash.....	8.3%

The original shipment weighed 85 tons and cost \$425.00. Calculate the loss in weight of the shipment and the actual cost per ton of the coal as sold.

Basis of Calculation: The amount of moisture-free coal in the load = 85×0.921 = 78.3 tons

Weight of coal as sold = $78.3/0.96$	81.5 tons
Loss in weight = $85 - 81.5$	3.5 tons
Cost of coal as sold = $425/81.5$	\$5.22 per ton

Illustration 4 (Class 3). A solution in an evaporator contains 20% by weight of soluble solids, the remainder being water. After 120 lb of water are evaporated it is found that the solution contains 28% soluble solids. Calculate the weight of the solution originally present in the evaporator.

Basis of Calculation: x lb of soluble solids present in solution.

Weight of the original solution.....	$x/0.20$
Weight of the final solution.....	$x/0.28$
Loss in weight = 120 lb =	$x/0.20 - x/0.28$

Solving: $x = 84$ lb

Weight of original solution = $84/0.20 = 420$ lb

Weight Balance. In essence the basis of any calculation involving changes in the composition and distribution of matter is a weight balance, which is a statement in ledger form wherein the initial weight is balanced against the final weight. This balance may be applied to the total mass involved, to each component in the process which passes through unchanged chemically, or to each chemical element present. A weight balance is essentially a statement of the principle of the conservation of mass. In solving a problem by this method the ease of calculation and the reliability of results depend upon the particular item or group of items chosen as the basis of the balance. This selection rests upon a knowledge of the relative magnitude and accuracy of the various items in the data supplied, and hence personal judgment and analytical experience may be required.

The three classes of problems illustrated above may be solved by the principle of the weight balance differing in the three cases by the selection of the basic component. In Illustration 2, the moisture-free coal was employed as the basis of calculation. A complete weight balance for each component and total weight follows:

Original Weights

Volatile matter (0.352) (85).....	29.9 tons
Fixed carbon (0.488) (85).....	41.5 tons
Ash (0.081) (85).....	6.9 tons
<hr/>	
Moisture-free coal.....	78.3 tons
Moisture (0.079) (85).....	6.7 tons
<hr/>	
Total coal.....	85.0 tons

Final Weights

Volatile matter.....	29.9 tons
Fixed carbon.....	41.5 tons
Ash.....	6.9 tons
<hr/>	
Moisture-free coal.....	78.3 tons
Moisture in coal $\frac{(0.04)(78.3)}{0.96}$	3.26 tons
<hr/>	
Total coal.....	81.56 tons
Moisture evaporated.....	3.44 tons
<hr/>	
Total.....	85.00 tons

It will be noted that the total weight balance includes balances of volatile matter, fixed carbon, ash, and moisture. Any one of these items could be taken as the basis for solving the problem, but in this instance the greatest accuracy and simplicity were obtained by choosing the moisture-free coal since this is the substance of greatest proportion and is determined easily with high accuracy. Experimentally the moisture determination alone is sufficient provided loss of moisture is the only change involved in storage. The problem could also have been solved from experimental data on the determination of carbon, hydrogen, nitrogen, or any other element in coal, but obviously this would involve unnecessary experimental analysis and less accuracy.

Compounding of Mixtures. It is frequently desired to prepare a mixture or solution of specified composition by the mixing of solutions or mixtures, each of which may contain two or more components in varying proportions. For example, a dilute aqueous solution of hydrochloric acid may be strengthened by the addition of concentrated acid which also contains some water. The proportions in which the two aqueous acids must be mixed in order to produce a solution of specified intermediate composition may be calculated algebraically, using a unit quantity of the final mixture as the basis. The weight of the final mixture must equal the sum of the weights of the mixtures which are combined in its formation. Furthermore, the weight of each pure component in the final mixture must be equal to the sum of the weights of that com-

ponent in all the mixtures which are combined to form the final mixture. These equalities may be represented by algebraic equations in terms of the weights and percentage compositions of the various mixtures.

Illustration 5. A tank of dilute hydrochloric acid contains 18% HCl by weight. Calculate the weight of concentrated acid, containing 40% HCl, which must be added to 100 lb of the dilute acid in order to raise the concentration to 28% HCl.

Basis: 100 lb of final 28% acid.

Let x = weight of 18% acid.

y = weight of 40% acid.

Writing a weight balance of all materials entering and leaving the mixing process:

$$x + y = 100 \quad (a)$$

Weight balance of HCl:

$$0.18x + 0.40y = 100 \times 0.28 = 28 \quad (b)$$

Solving (a) and (b) simultaneously:

$$0.18(100 - y) + 0.40y = 28$$

$$0.22y = 10$$

$$y = 45.5 \text{ lb of 40\% acid}$$

$$x = 54.5 \text{ lb of 18\% acid}$$

Weight of 40% acid per 100 lb of 18% acid =

$$\frac{45.5}{54.5} \times 100 = 83.5 \text{ lb}$$

The problem is more complicated if it is desired to prepare a mixture of three or more components by compounding individual mixtures which already contain two or more of the components. For example, in nitrating processes a "mixed acid" is used which contains H_2SO_4 , HNO_3 , and water. The waste acid from a process is strengthened for reuse by the addition of concentrated aqueous HNO_3 and H_2SO_4 . The necessary proportions in which the materials must be mixed in order to produce a specific mixed acid may be calculated by the same general method used in Illustration 5. Algebraic equations are written to represent the weight balance of all materials entering and leaving the mixing process and also the weight balances of each of the pure components. These equations are then solved algebraically.

Illustration 6. The waste acid from a nitrating process contains 23% HNO_3 , 57% H_2SO_4 , and 20% H_2O by weight. This acid is to be concentrated to contain 27% HNO_3 and 60% H_2SO_4 by the addition of concentrated sulphuric acid containing 93% H_2SO_4 and concentrated nitric acid containing 90% HNO_3 . Calculate the weights of waste and concentrated acids which must be combined to obtain 1000 lb of the desired mixture.

Basis: 1000 lb of final mixture.

Let x = weight of waste acid

y = weight of conc. H_2SO_4

z = weight of conc. HNO_3 .

Weight balance of all materials:

$$x + y + z = 1000 \quad (a)$$

Weight balance of H_2SO_4 :

$$0.57x + 0.93y = 1000 \times 0.60 = 600 \quad (b)$$

Weight balance of HNO_3 :

$$0.23x + 0.90z = 1000 \times 0.27 = 270 \quad (c)$$

Equations (a), (b), and (c) may be solved simultaneously.

Eliminating z from (a) and (c):

$$\frac{270 - 0.23x}{0.90} = y + z$$

or

$$y + 0.744x = 700 \quad (d)$$

Eliminating y from (d) and (b):

$$0.57x + 0.93(700 - 0.744x) = 600$$

$$0.122x = 51$$

$$x = 418 \text{ lb}$$

From (b)

$$y = \frac{600 - 0.57 \times 418}{0.93} = 390 \text{ lb}$$

From (a)

$$z = 1000 - 390 - 418 = 192 \text{ lb}$$

These results may be verified by a weight balance of the water in the process.

$$\text{Water entering} = (418 \times 0.20) + (390 \times 0.07) + (192 \times 0.10) = 130 \text{ lb}$$

Since the final solution contains 13% H_2O , this result verifies the calculations.

More complicated problems may be handled by the same type of analysis. Where more than two simultaneous equations are to be solved considerable simplification results from the use of determinants. In this way a general equation may be derived which permits simple routine solutions where a large number of problems of the same type are to be solved. The advantages of this method were stressed in a paper by Deatrick.¹

Conversion of Units, Symbols, and Equations. The conversion of units and symbols from one system to another often presents a troublesome operation in technical calculations. After training in the use of metric units in the basic courses of physics and chemistry many difficulties are experienced in translating such information into the units employed in American industries; in Europe this handicap is not suffered. Both the metric and English units are intentionally employed in this book in order to bridge the gap between scientific training and industrial application.

In nearly every handbook tables of conversion factors will be found, and these are recommended for use whenever available and adequate.

¹ Ind. Eng. Chem. **23**, 34 (1931).

CONVERSION OF UNITS, SYMBOLS,

A few simple rules will be given for guidance when conversion factors becomes necessary.

Most scientific units may be expressed in terms such as length, weight, time, temperature, and heat. In conversion the unit is first expressed in terms of its simplest dimensions combined with the known numerical or symbolic value of the unit. Thus, the viscosity of a liquid is μ grams per second-centimeter. In the English system the value will be expressed in pounds per second-foot. Each of the dimensions is replaced separately by the dimension of the desired system together with its corresponding conversion factor. Thus, since 1 gram = 0.002204 lb and 1 cm = 0.0328 ft

$$\frac{\text{grams}}{(\text{sec})(\text{cm})} = \mu \frac{0.002204 \text{ lb}}{1 (\text{sec}) 0.0328 (\text{ft})} = 0.0670 \mu \frac{\text{lb}}{(\text{sec})(\text{ft})}$$

Similarly a pressure of 1 atmosphere =

$$\frac{14.7 \text{ lb}}{(\text{in.})^2} = \frac{14.7 (453.6) \text{ grams}}{(2.54)^2 (\text{cm})^2} = 1035 \frac{\text{grams}}{(\text{cm})^2}$$

since 1 lb = 453.6 grams and 1 in. = 2.54 cm

The gas constant R =

$$\frac{82.06 (\text{atm})(\text{cm})^3}{(\text{gram mol})(^\circ\text{K})} = \frac{(82.06) (1 \text{ atm}) (0.0328 \text{ ft})^3}{(0.002205 \text{ lb-mol}) (1.8^\circ\text{R})} = 0.729 \frac{(\text{atm})(\text{ft})^3}{(\text{lb-mol})^\circ\text{R}}$$

Also since 1 atmosphere = 14.7 lb per in.² = 14.7 \times 144 or 2120 lb per ft²,

$$R = \frac{(0.729) (2120 \text{ lb/ft}^2) (\text{ft})^3}{(\text{lb-mol})(^\circ\text{R})} = 1540 \frac{(\text{ft})(\text{lb})}{(\text{lb-mol})(^\circ\text{R})}$$

Conversion of Equations. When an equation is so expressed that all dimensions cancel out when substituted for the given units the equation is said to be dimensionless or dimensionally homogeneous. Such an equation remains unaltered in form and in its coefficients regardless of the system of units employed provided similar dimensions are expressed consistently in the same units. Thus the following equation in heat transmission is dimensionless and will remain unaltered in form and coefficient for any consistent system of units.

$$h = 0.023 \frac{k}{x} \left(\frac{c\mu}{\tau} \right)^{1/3} \left(\frac{dG}{\tau} \right)$$

To prove that this equation is dimensionless, consistent dimensions are substituted for the various symbols, thus

h , heat-transmission coefficient,	$\frac{\text{Btu}}{(\text{ft})^2}$
k , thermal conductivity,	$\frac{\text{Btu}}{(\text{hr}) (\text{ft}) (^\circ\text{F})}$
μ , viscosity,	$\frac{\text{lb}}{(\text{hr}) (\text{ft})}$
G , mass velocity,	$\frac{\text{lb}}{(\text{hr}) (\text{ft})^2}$
c , heat capacity,	$\frac{\text{Btu}}{(\text{lb})}$
d , diameter,	ft

Substituting,

$$\frac{\text{Btu}}{(\text{hr}) (\text{ft})^2 (^\circ\text{F})} \cdot \frac{\frac{\text{Btu}}{(\text{hr}) (\text{ft}) (^\circ\text{F})}}{\text{ft}} \frac{(\text{Btu}) (\text{lb})}{(\text{lb}) (^\circ\text{F}) (\text{hr}) (\text{ft})}^{1/3} \frac{(\text{ft}) (\text{lb})}{(\text{ft})}^{0.8}$$

Collecting,

$$\frac{\text{Btu}}{(\text{hr}) (\text{ft})^2} \cdot \frac{\text{Btu}}{(\text{hr}) (\text{ft})^2 (^\circ\text{F})} \left[\frac{(\text{Btu}) (\text{lb}) (\text{hr}) (\text{ft}) (^\circ\text{F})}{(\text{Btu}) (\text{lb}) (\text{hr}) (\text{ft}) (^\circ\text{F})} \right]^{1/3} \left[\frac{(\text{ft})^2 (\text{lb}) (\text{hr})}{(\text{ft})^2 (\text{lb}) (\text{hr})} \right]^{0.8}$$

The following equation is empirical and not dimensionless; furthermore, the dimensions used are not consistent but chosen for convenience in magnitude. It is desired to transform this equation into other, arbitrary units which may or may not be consistent. Any transformation of units will alter the coefficient.

$$\frac{0.22 \, c T G^{0.8}}{D^{0.2}}$$

h , heat-transmission coefficient,	$\frac{\text{Btu}}{(\text{hr}) (\text{ft}) (^\circ\text{F})}$
c , heat capacity,	$\frac{\text{Btu}}{(\text{lb}) (^\circ\text{F})}$
T , temperature,	$^\circ\text{R}$
G , mass velocity,	$\frac{\text{lb}}{(\text{hr}) (\text{ft})^2}$
D , diameter,	in.

It is desired to transform this equation into new units, as follows,

$$h_1 = \alpha \frac{c_1 T_1 G_1^{0.8}}{D_1^{0.2}} \quad (2)$$

where α is the new coefficient,

$$h_1, \frac{\text{kg cal}}{(\text{hr}) (\text{m})^2 (^\circ\text{C})}$$

$$c_1 \frac{\text{kg cal}}{(\text{kg}) (^\circ\text{C})}$$

$^\circ\text{K}$

$$G_1, \frac{\text{kg}}{\text{cm}}$$

cm

$$\text{now } h_1 \frac{\text{kg cal}}{(\text{hr}) (\text{m})^2 (^\circ\text{C})} = \frac{h_1 (3.968 \text{ Btu})}{(1 \text{ hr}) (3.28 \text{ ft})^2 (1.8^\circ\text{F})} = h \frac{\text{Btu}}{(\text{hr}) (\text{ft})^2 (^\circ\text{F})}$$

$$\text{or } h = 0.2045 h_1$$

$$\frac{(\text{kg cal})}{(\text{kg}) (^\circ\text{C})} \quad \frac{(3.968 \text{ Btu})}{(2.204 \text{ lb}) (1.8^\circ\text{F})} = c \frac{\text{Btu}}{(\text{lb}) (^\circ\text{F})} \quad \text{or } c =$$

$$G_1 \frac{\text{kg}}{(\text{hr}) (\text{m})^2} = G_1 \frac{2.204 \text{ lb}}{(1 \text{ hr}) (3.28 \text{ ft})^2} = G \frac{\text{lb}}{(\text{hr}) (\text{ft})^2} \quad \text{or } G = 0.204 G_1$$

$$^\circ\text{K} = (1.8 T_1) ^\circ\text{R} = T ^\circ\text{R} \quad \text{or } T = 1.8 T_1$$

$$= (0.3937 D_1) \text{ in.} = D \text{ in.} \quad \text{or } D = 0.3937$$

Substituting in Equation (1)

$$0.2045 h_1 = 0.22 \quad (0.3937 D_1)^{0.2}$$

$$\text{or } = 6.52 \quad (3)$$

$$= 6.52$$

Equations (1) and (3) are now identical.

When the values of the Centigrade or Fahrenheit temperature scale appear in an equation the following conversion is used,

$$t = \frac{t_f}{1.8}$$

where

t is in degrees Centigrade

t_f is in degrees Fahrenheit

Thus the molal heat capacity of CO_2 gas is given by the equation

$$C_p = [9.085 + 0.0048 t - 0.83 \times 10^{-6} t^2] \frac{\text{C}}{(\text{mol}) (^\circ\text{C})}$$

This equation is changed as follows to obtain C_p in Btu per lb- $^\circ\text{F}$.

The molecular weight of CO_2 is 44. Converting the value of heat capacity in Btu per lb- $^{\circ}\text{F}$,

$$C_p \frac{\text{Cal}}{(\text{kg-mol})(^{\circ}\text{C})} = C_p \frac{3.968 \text{ Btu}}{(44)(2.204 \text{ lb})(1.8^{\circ}\text{F})} = C_p \frac{\text{Btu}}{(\text{lb})(^{\circ}\text{F})} \quad \text{or} \quad C_p = 0.0227 C_p$$

Hence

$$0.0227 \left[9.085 + 0.0048 \left(t_f - 0.83 \times 10^{-6} \left(\frac{t_f - 32}{1.8} \right)^2 \right) \right] \text{ Btu}$$

or $C_p = [0.2041 + 0.609 \times 10^{-4} t_f - 0.584 \times 10^{-8} t_f^2] \frac{\text{Btu}}{(\text{lb})(^{\circ}\text{F})}$

PROBLEMS

Tables of Common Atomic Weights and Conversion Factors will be found in the Appendix, pages 471-473

- A solution contains 10% sodium chloride and 90% water, by weight.
 - The solution is evaporated until 30% of the water is removed. Calculate the composition of the remaining solution.
 - Calculate the amount of water which must be evaporated from 1000 lb of the original solution in order to concentrate it to 20% NaCl by weight.
 - Calculate the percentage of the water originally present which must be removed in order to concentrate the solution to 30% NaCl by weight.
- After drying, a batch of leather is found to weigh 900 lb and to contain 7% of moisture. During drying the leather lost 59.1% of its original weight when wet.
 - Calculate the percentage of "bone-dry" or "moisture-free" leather in the original wet stock.
 - Calculate the number of pounds of water removed in the drying process per pound of bone-dry leather.
 - Calculate the percentage of the water originally present which was removed in the drying process.
- A coal sample, received for analysis, loses 4% of its original weight on exposing it to the air for 30 hours. The analysis of the remaining "air-dried" coal was found to be: 40% volatile matter, 50% fixed carbon, 3% moisture, and 7% ash:
 - Assuming that all the loss in air drying was moisture, calculate the analysis of the sample "as received."
 - The fixed carbon and the volatile matter form what is termed the "combustible" of the coal. Calculate the analysis of the combustible of this coal.
 - Calculate the number of pounds of water which might be removed by air drying enough of this coal to produce 1.0 ton of the air-dried product.
- In the manufacture of soda-ash by the LeBlanc process, sodium sulphate is heated with charcoal and calcium carbonate. The resulting "black ash" has the following composition:

Na_2CO_3	42%
Other water-soluble material.....	6%
Insoluble material (charcoal, CaS, etc.).....	52%

The black ash is treated with water to extract the sodium carbonate. The solid residue from this treatment has the following composition:

NaCO ₃	4%
Other water-soluble salts.....	0.5%
Insoluble matter.....	85%
Water.....	10.5%

- a. Calculate the weight of residue remaining from the treatment of 1.0 ton of black ash.
 - b. Calculate the weight of sodium carbonate extracted per ton of black ash treated.
5. As dug from the ground, peat has the following composition:

Moisture.....	88.0%
Volatile matter.....	8.05%
Fixed carbon.....	3.18%
Ash.....	0.77%

For use as a domestic fuel this peat is dried until it contains only 10% water. A process for drying by artificial heat is developed whereby water may be evaporated at a cost of 2.5 cents per 100 lb of water removed. Calculate the drying cost per ton of product.

6. A furnace is fired with coal containing 4.1% moisture, 31.8% volatile matter, 56.2% fixed carbon, and 7.9% ash. The refuse removed from the pit has the following composition:

Volatile matter.....	6.2%
Fixed carbon.....	27.1%
Ash.....	66.7%

- a. Calculate the weight of refuse formed per ton of coal burned.
- b. Calculate the percentage of the total combustible matter which is lost in the refuse.

7. It is desired to measure the rate at which waste gases are passing up a stack. The gases entering contain 2.1% carbon dioxide by weight. Pure carbon dioxide is introduced into the bottom of the stack at a measured rate of 4.0 lb per minute. It is found that the gases leaving the stack contain 3.2% carbon dioxide by weight. Calculate the rate of flow, in pounds per minute, of the entering waste gases.

8. A contract is drawn up for the purchase of paper containing 5% moisture at a price of 7 cents per pound. It is provided that if the moisture content varies from 5%, the price per pound shall be proportionately adjusted in order to keep the price of the bone-dry paper constant. In addition, if the moisture content exceeds 5%, the purchaser shall deduct, from the price paid the manufacturer, the freight charges incurred due to the excess moisture. If the freight rate is 90 cents per 100 lb, calculate the price to be paid for 3 tons of paper containing 8% moisture.

9. A laundry can purchase soap containing 30% of water at a price of \$7.00 per 100 lb f. o. b. the factory. The same manufacturer offers a soap containing 5% of water. If the freight rate is 60 cents per 100 lb, what should the laundry pay the manufacturer for the 5% soap?

10. Raw silk contains three natural components, pure fiber, moisture, and a protective coating of sericin. In the process of "throwing," the silk is soaked in an emulsion by which various reagents are added to the raw material. The resulting combination of sericin and addition reagents is known as the "boil-off" content.

The pure fiber is unaffected in quantity by the throwing process. The moisture content of silk is universally expressed in percentage by weight of the dry, moisture-free material. The sericin content of raw silk is expressed in percentage by weight of the moisture-free raw silk. The "boil-off" content of thrown silk is expressed in percentage by weight of the moisture-free thrown silk.

The price of thrown silk is usually quoted on the basis of a moisture content of 11% and a boil-off content of 23%. For the determination of actual selling prices the pure fiber is the only component regarded as valuable. No penalty for the presence of excess moisture or boil-off content is applied to the price per unit weight of pure fiber.

The chemical analysis of a sample of silk is as follows, the percentages being based on the total weight of the sample as received:

Moisture.....	10.2%
Boil-off content.....	24.0%
Fiber.....	65.8%

Calculate the composition of this sample as expressed in the standard terms of the silk industry.

11. Raw Japanese silk has the following average composition, expressed on the standard bases described in Problem 10.

Moisture.....	11%
Sericin.....	18.5%

From it is prepared thrown silk of the following composition expressed on the standard bases.

Moisture.....	10%
Boil-off content.....	21%

Calculate the weight of dry reagents which were absorbed by 1 lb of raw silk in the soaking process.

12. If the quoted, basic price of thrown silk is \$3.00 per lb, calculate the selling price of the thrown silk of Problem 11.

13. The spent acid from a nitrating process contains 43% H_2SO_4 , 36% HNO_3 , and 21% H_2O by weight. This acid is to be strengthened by the addition of concentrated sulphuric acid containing 91% H_2SO_4 , and concentrated nitric acid containing 88% HNO_3 . The strengthened mixed acid is to contain 40% H_2SO_4 and 43% HNO_3 . Calculate the quantities of spent and concentrated acids which should be mixed together to yield 1000 lb of the desired mixed acid.

14. The waste acid from a nitrating process contains 23% HNO_3 , 57% H_2SO_4 , and 20% H_2O by weight. This acid is to be concentrated to contain 27% HNO_3 and 60% H_2SO_4 by the addition of concentrated sulphuric acid containing 93% H_2SO_4 and concentrated nitric acid containing 90% HNO_3 . Calculate the weights of waste and concentrated acids which must be combined to obtain 1000 lb of the desired mixture.

15. A dry black ash contains 1000 lb of sodium carbonate and 1000 lb of insoluble sludge. The sodium carbonate is to be extracted from this ash with 10,000 lb of water using three thickeners in series with countercurrent flow of sludge and water. The fresh water enters the third thickener, overflows to the second, and is then passed to an agitator where it is mixed with the black ash. The resultant sludge from the agitator is passed to the first thickener. The sludge is pumped from one thickener to the next and discharged as waste from the third thickener. The sludge holds

3 lb of water for each pound of insoluble matter as it leaves each thickener. The concentrated sodium carbonate is drawn off and recovered from the first thickener. Calculate the weight of sodium carbonate recovered, assuming that all sodium carbonate is entirely dissolved to form a uniform solution in each agitator.

16. Make the following conversion of units:

- An energy of 8 ft-lb to kilogram-meters.
- An acceleration of $32.2 \frac{\text{ft}}{(\text{sec})^2}$ to $\frac{\text{meters}}{(\text{sec})^2}$
- A pressure of 100 mm of Hg to inches of water.
- Thermal conductivity of $k \frac{\text{Btu}}{(\text{hr}) (^\circ\text{F}) (\text{ft})}$ to $\frac{\text{kg cal}}{(\text{hr}) (^\circ\text{C}) (\text{m})}$.
- The gas constant R , from $\frac{82.06 (\text{atm}) (\text{cm})^3}{(\text{g-mol}) (^\circ\text{R})}$ to $\frac{\text{Btu}}{(\text{lb-mol}) (^\circ\text{R})}$.

17. Transform the following equation into a dimensionless form:

$$h = \frac{0.020k}{D} \left(\frac{DG}{\mu} \right)^{0.8}$$

where

$$\frac{\text{Btu}}{(\text{hr}) (\text{ft})^2 (^\circ\text{F})}$$

$$k, \frac{\text{Btu}}{(\text{hr}) (\text{ft}) (^\circ\text{F})}$$

$$D, \text{ ft.}$$

$$G, \frac{\text{lb}}{(\text{hr}) (\text{ft})^2}$$

$$\mu, \frac{\text{lb}}{(\text{hr}) (\text{ft})}$$

What would be the numerical value of the coefficient with consistent metric units?

CHAPTER II

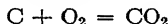
STOICHIOMETRY

According to generally accepted theory, elementary matter is composed of submicroscopic particles of the chemical elements known as atoms. It is postulated that all atoms of a single element are of the same average weight but that atoms of different elements have characteristically different average weights.¹ Chemical compounds are formed by the union of definite numbers of atoms of various elements to form groups termed molecules. Although the actual numbers of atoms present in molecules are frequently uncertain, the relative numbers of the atoms of different elements will be expressed by simple integers and will be constant and definite for any specific compound. For example, the size of the water molecule in the liquid state is open to discussion, but it is definitely known that for each atom of oxygen present there will always be two atoms of hydrogen. From the relative weights in which elements combine to form compounds it is possible to determine the relative weights of the atoms themselves. The international atomic weights form such a scale, merely expressing the relative weights of the elements, referred to the arbitrarily assigned value of 16.00 to represent the relative weight of the oxygen atom. Since these atomic weights are proportional to the weights of the atoms, it follows that *masses of different elements which bear the same weight ratios to each other as the atomic weight numbers of the elements must all contain the same number of atoms*. Thus, for example, the number of grams of an element corresponding to its atomic weight number will contain a perfectly definite number of atoms, and this number will be the same for all elements. This quantity of an element corresponding in grams to the atomic weight number has been designated as one *gram-atom*, representing a definite, constant number of primary atoms. The number of single atoms in one gram-atom of any element has been determined by several methods, the average result being 6.06×10^{23} . This very important constant is termed the Avogadro number.

¹ Since the discovery of isotopes it is commonly recognized that the individual atoms of certain elements may vary in the weight, and that so-called atomic weight of the element is the weighted average of the atomic weights of the isotopes of which the element is composed.

The formula of a chemical compound, on the basis of the atomic theory, indicates the relative numbers and kinds of atoms uniting in its formation. Thus, the formula NaCl indicates that one atom of sodium has united with one atom of chlorine. It also follows, since the gram-atom contains a definite number of atoms, the same for all elements, that gram-atoms will unite to form a compound in the same ratios as do the atoms themselves, forming what may be termed a *gram-molecule* of the compound. One gram-molecule represents the weight in grams of all the gram-atoms which, in the formation of the compound, combine in the same numbers as do the single atoms in the formation of a single molecule. Very frequently the actual number of gram-atoms in a gram-molecule is unknown or is so large as to be cumbersome. In such cases the *gram-formula-weight* is a more desirable unit than the gram-molecule. Where the molecular weight is uncertain the gram-formula-weight usually represents the weight of the smallest number of gram-atoms which will combine in the ratios required in the compound. For example, the molecular weight or weight of a gram-molecule of cellulose, $(\text{C}_6\text{H}_{10}\text{O}_5)_x$, is unknown, but one gram-formula-weight would be 162 grams, as represented by the above formula where x is unity. Because of the cumbersome nature of the term gram-formula-weight it will be replaced by the convenient term *gram-mol*, which will be used as synonymous with it.

The chemical equation may be considered as representing the relative numbers of gram-atoms and gram-mols entering into a reaction. As a specific illustration the following simple reaction may be considered:



This equation signifies that one atom of carbon will combine with two atoms of oxygen to form one molecule of carbon dioxide. It also indicates that one gram-atom of carbon will combine with one gram-mol of oxygen to form one gram-mol of carbon dioxide. Although the weight of the atom or the molecule is an extremely small quantity, the gram-atom or gram-mol represents a measurable amount of material capable of serving as a unit for practical calculations. It is therefore convenient to adopt such units for the expression of quantities of chemically reacting materials. Such unit quantities will always react with each other in simple, integral multiples.

In addition to gram-atoms and gram-mols it is convenient to use units similarly defined in other systems of measurement. Thus, the term *pound-atom* represents a quantity of an element having a weight equal to its atomic weight number in pounds. Similarly, the *pound-mol* represents a quantity of a compound having a weight in pounds which is equal to its formula weight.

The Use of Molal Units. The pound-mol forms a unit of quantity which is of great convenience in the solution of all types of problems concerned with the reactions and properties of definite chemical compounds of known compositions. The actual significance of the molal units must be kept clearly in mind. From the definition, it is apparent that one pound-mol of a material represents a perfectly definite and tangible quantity. Thus 1 pound-mol of sodium chloride weighs 58.45 pounds and contains a definite number of atoms of sodium and chlorine. Exactly the same number of atoms of sulphur will be contained in one pound-mol of sulphuric acid, which weighs 98.08 pounds. Any quantity of such a material may be expressed in terms of the number of pound-mols which it represents, just as it might be expressed in terms of kilograms, tons, or any other units of quantity. Thus, 100 pounds of sodium chloride are $100/58.45$ or 1.71 pound-mols. Similarly, 1 ton of 100 per cent sulphuric acid is $2000/98.08$ or 20.4 pound-mols. Conversely, 1.5 pound-mols of 100 per cent sulphuric acid refer to a quantity weighing 1.5×98.08 or 147 pounds.

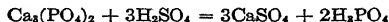
The great desirability of the use of molal units for the expression of quantities of chemical compounds cannot be overemphasized. Since one molal unit of one compound will always react with a simple multiple number of molal units of another, calculations of weight relationships in chemical reactions are greatly simplified if the quantities of the reacting compounds and products are expressed throughout in molal units. This simplification is not important in very simple calculations, centered about a single compound or element. Such problems are readily solved by the means of the combining weight ratios, which are commonly used as the desirable means for making such calculations as may arise in quantitative analyses. However, in an industrial process successive reactions may take place with varying degrees of completion, and it may be desired to calculate the weight relationships of *all* the materials present at the various stages of the process. In such problems the use of ordinary weight units with combining weight ratios will lead to great confusion and opportunity for arithmetical error. The use of molal units, on the other hand, will give a more direct and simple solution in a form which may be easily verified. It is urged as highly advisable that familiarity with molal units be gained through their use in *all* calculations of weight relationships in chemical compounds and reactions.

A still more important argument for the use of molal units lies in the fact that many of the physicochemical properties of materials are expressed by simple laws when these properties are on the basis of a molal unit quantity. Thus, such properties as the heat of vaporization, the heat capacity, and the gaseous volume, *per molal unit of quantity*, are

expressed by simple relationships applying to a variety of different materials. These same properties apparently follow no regular laws when expressed on the basis of unit weights of the materials.

Illustration 1. Phosphoric acid, H_3PO_4 , is prepared by treating calcium phosphate with the theoretically required quantity of sulphuric acid. Calculate the weight of the calcium phosphate used and the weights of each of the products formed, per 100 lb of sulphuric acid.

Solution:



This equation signifies that 1 lb-mol of calcium phosphate requires 3 lb-mols of sulphuric acid and will produce 3 lb-mols of calcium sulphate and 2 lb-mols of phosphoric acid.

Basis: 100 lb of H_2SO_4 .

Molecular weights:

$\text{Ca}_3(\text{PO}_4)_2$	310
H_2SO_4	98
CaSO_4	136
H_3PO_4	98

	H_2SO_4 present = 100/98.....	1.02 lb-mols
	$\text{Ca}_3(\text{PO}_4)_2$ required = $1.02 \times \frac{1}{3}$	0.34 lb-mol
or	0.34×310	105 lb
	CaSO_4 formed = 1.02 lb-mols,	
or	1.02×136	139 lb
	H_3PO_4 formed = $1.02 \times \frac{2}{3}$	0.68 lb-mol
or	0.68×98	66 lb

Weight Balance:

Total weight of reactants, 100 + 105.....	205 lb
Total weight of products, 139 + 66.....	205 lb

It is seen that in this type of solution the molecular weight of each compound appears only once in the entire calculation. In the solution of the same problem in weight units with combining weight ratios, a new ratio would be set up for each step, adding to the complexity and chances for error.

Composition by Weight of Chemical Compounds. From the atomic weight data the composition by weight of a chemical compound of known formula may readily be calculated. The calculation may be based on one gram-mol of the compound, the weight of which is thereby known. In this quantity are present one or more gram-atoms of each of the elements making up the molecule. From the weights of the various gram-atoms the weight-percentages which are formed by any of the elements or groups of elements may be calculated.

Illustration 2. Calculate the percentage of oxygen, by weight, present in sulphuric acid (H_2SO_4).

<i>Basis:</i> 1 gram-mol of H_2SO_4	98.1 grams
4 gram-atoms of oxygen = 4×16	64 grams
Percentage oxygen = $100 (64/98.1)$	65.2%

INDUSTRIAL CHEMICAL REACTIONS

Excess Reactants. The principles outlined above permit the solution of many problems involved in industrial reaction processes. However, in ordinary practice the quantities of reacting compounds and products actually present do not follow the proportions indicated by the equation theoretically representing the reaction. It is generally desirable that some of the reacting materials be present in excess of the amounts theoretically required for combination with the others. Under such conditions the products obtained will contain some of the uncombined reactants. The quantities of the desired compounds which are formed in the reaction will be determined by the quantity of the *limiting reactant*, that is, the material which is not present in excess of that required to combine with any of the other reacting materials. The amount by which any reactant is present in excess of that required to combine with the limiting reactant is usually expressed as its *percentage excess*. The percentage excess of any reactant is defined as the percentage ratio of the excess to the amount theoretically required for combination with the limiting reactant.

Degree of Completion. Even though certain of the reacting materials may be present in excess, many industrial reactions do not proceed to the extent which would result from the complete reaction of the limiting material. Such partial completion may result from the establishment of an equilibrium in the reacting mass or from insufficient time or opportunity for completion to the theoretically possible equilibrium. The *degree of completion* of a reaction is ordinarily expressed as the percentage of the limiting reacting material which is entirely converted into the desired products. In processes in which two or more successive reactions of the same materials take place, the degree of completion of each step may be separately expressed.

Reactions Having a Single Product. In industrial processes, even though the reaction be complete, the products will generally contain some of the reacting materials, whereas in an incomplete reaction all the original reacting materials will appear in various amounts in the product. It is of interest that the relationships existing between the weights and compositions of the mass of reacting materials and those of the products may be calculated under any specified conditions. Most of the problems of this type which ordinarily arise are of two general classes.

1. The compositions and weights of the materials entering a reaction process are known. It is required to calculate the compositions and

weights of the products resulting from a specified degree of completion of the reaction.

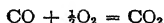
2. The compositions and weights of the reacting materials and of the products of a reaction are partially known. It is required to calculate the complete compositions of both reactants and products and to determine the degree of completion of the reaction.

It is desirable in all calculations dealing with definite chemical reactions to express the quantities of the materials capable of actually reacting, in terms of molal units. Since data are not ordinarily presented in molal form, the first step in the solution of such problems will be the conversion of the specified quantities of the *active components* into molal units.

Problems of the first group are readily solved by first converting into molal units the weights of the reacting compounds present in a unit weight of the materials. From inspection of these quantities the reacting compound which limits the extent of the reaction may be selected if it is not specified. If the quantity of the limiting reactant is designated the quantity of each of the other reacting materials may be specified in terms of the percentage excess it forms of that theoretically required. The actual weight of these materials, expressed in molal units, may be calculated from a knowledge of the theoretical reaction. The calculation may then be completed on the basis of the quantity of the limiting reactant which is present in a unit mass of the materials entering the reaction. The amounts of the new products formed in the reaction are determined by the degree of completion, while the unconsumed reacting substances and inert materials will pass into the final product unchanged. The method of solution is demonstrated in the following illustration:

Illustration 3. A producer gas made from coke has the following composition by weight: CO, 27.3%; CO₂, 5.4%; O₂, 0.6%; N₂, 66.7%. This gas is burned with such a quantity of air that the oxygen present is 20% in excess of that required to combine with the combustible material. If the combustion were 98% complete, calculate the weight and composition of the gaseous products formed per 100 lb of gas burned.

Solution:



Basis of Calculation: 100 lb of the original producer gas.

CO present = 27.3 lb or	0.975 lb-mol
Oxygen required for combustion = $0.975/2$	0.487 lb-mol
Oxygen supplied for 20% excess = 1.2×0.487	0.585 lb-mol
Oxygen already present in gas = $0.6/32$	0.019 lb-mol
Oxygen to be supplied from air = 0.566 lb-mol or	18.1 lb
Weight of air used = $18.1/0.232$	78.2 lb
Weight of nitrogen introduced = $78.2 - 18.1$	60.1 lb

CO ₂ formed in combustion = $0.98 \times 0.975 = 0.955$ lb-mol or.....	42.1 lb
O ₂ consumed in combustion = $0.487 \times 0.98 = 0.477$ lb-mol.....	15.3 lb
Total N ₂ present in gases = $60.1 + 66.7$	126.8 lb
Total CO ₂ present in gases = $42.1 + 5.4$	47.5 lb
Total O ₂ present in gases = $18.1 + 0.6 - 15.3$	3.4 lb
CO present in gases = 0.02×27.3	0.5 lb
Total weight of gases (as check).....	178.2 lb
Total weight of gas + air used.....	178.2 lb

Composition of gases by weight:

CO ₂	26.6%
O ₂	1.9%
CO.....	0.3%
N ₂	71.2%
	<hr/> 100.0%

The solution of a problem of the second class resolves itself into the apportionment among the products and the original materials of each element or radical which is present. It is necessary that the total quantity be known of each element and radical which is present in the process. This information may be derived from knowledge of the compositions of either the original materials or of the final products. In addition, a certain amount of knowledge is necessary regarding the distribution of the elements and radicals among the compounds of the original materials and of the products. For example, each element or radical present in the reaction may appear in two or more different compounds, both in the original materials and in the products. In order to determine the relative quantities of the various compounds it is then necessary to know the proportions in which at least one of the common elements is distributed among them. Knowledge of the distribution of one element may permit calculation of the quantities present of some of the compounds. From these results the distribution of other elements may be calculated and a complete solution built up from a minimum amount of initial information.

All such stoichiometric calculations are based on the law of the conservation of mass, which states that the total mass of any element or group of elements which enters a process is equal to the total masses of these same materials which leave the process or are retained therein. As discussed in Chapter I, an expression of the equality of the initial and final masses of any element or group of elements is termed a *weight balance*. If all items except one of such a weight balance are known, this item may be determined by difference, thus completing the balance.

The concept of the weight balance is a most useful means of calculating the complete distribution of an element or group of elements among the various materials of a process. The complete solution of an intricate stoichiometric problem thus resolves itself into a series of weight balances.

As a basis of calculation for problems of the second class it is convenient to select a unit weight of either the original or final material, depending on the manner in which the data are presented. The quantities of all materials which are active in the reaction are best expressed in molal units. The following illustrations show methods of procedure for the solution of two typical problems of this class.

Illustration 4. For the preparation of ferrous sulphide (FeS) 3 parts of iron filings are heated with 2 parts of sulphur. The product from such a process is found to contain 60% FeS .

a. Calculate the complete analysis of the product, assuming that no sulphur is lost and no other sulphides of iron are found.

b. Determine the limiting reactant and calculate the percentage excess of the other reactant in the original charge.

c. Calculate the degree of completion of the reaction.

Basis: 100 lb of products = 100 lb of original material.

FeS in product = 60 lb or 60/87.9.....	0.683 lb-mol
Total Fe present = 60 lb.....	1.075 lb-atoms
Total S present = 40 lb.....	1.250 lb-atoms
Fe in FeS = 0.683×55.8	38.1 lb
S in FeS = 0.683×32.0	21.9 lb
Excess Fe = $60 - 38.1$	21.9 lb
Excess S = $40 - 21.9$	18.1 lb

a. Analysis of product:

FeS.....	60.0%
Fe.....	21.9%
S.....	18.1%
	<hr/>
	100.0%

b. Since 1.0 lb-atom of sulphur combines with 1.0 lb-atom of iron, the iron is the limiting reactant.

Sulphur theoretically required.....	1.075 lb-atoms
Excess sulphur, $1.250 - 1.075$	0.175 lb-atom
Percentage excess sulphur, $0.175/1.075$	16.3%

c. Of the 60 lb of iron, the limiting material, only 38.1 lb reacted.

Degree of completion = $38.1/60 = 63.5\%$

Illustration 5. A solution of sodium carbonate is causticized by the addition of partially slaked, commercial lime. The lime added contains only calcium carbonate as an impurity. A small amount of free caustic soda is present in the original solution. The mass obtained from the causticization has the following analysis:

CaCO_3	13.48%
CaO	0.21%
Na_2O	8.02%
Na_2CO_3	0.61%
H_2O	77.68%
	<hr/> 100.00%

Calculate:

- The composition of the initial reacting mass.
- The reacting material in excess and its percentage excess.
- The degree of completion of the reaction.

Solution: In this problem each component present in the reacting mass also appears in the products. It is evident that with the amount of data given the problem cannot be solved, since an infinite number of combinations of the carbonates and oxides in the reacting mass might result in products of this composition. No one element or radical of any of the reacting compounds can be definitely apportioned among the various types of compounds in which it was introduced. Some information as to the distribution of one of these elements in the reacting mass must therefore be supplied. The analysis of the dissolved material contained in the original solution to be causticized will determine the distribution, between the entering oxide and carbonate of all the sodium in the process. If this analysis is determined to be: Na_2O , 3.0%; and Na_2CO_3 , 97%; the calculation of the complete initial analysis may be completed.

Components of the original mixture:

H_2O
 CaO
 CaCO_3
 Na_2CO_3
 Na_2O

Distribution of Na in the original solution of Na_2CO_3 and Na_2O :

Basis: 100 lb of the dissolved Na_2CO_3 and Na_2O in the original solution.

$\text{Na}_2\text{O} = 3 \text{ lb or } 3/62$	0.0484 lb-mol
$\text{Na}_2\text{CO}_3 = 97 \text{ lb or } 97/106$	0.915 lb-mol
$\text{Na in Na}_2\text{O} = 2 \times 0.0484$	0.0968 lb-atom
$\text{Na in Na}_2\text{CO}_3 = 2 \times 0.915$	1.830 lb-atoms

Distribution of Na:

$\text{In Na}_2\text{O} = 0.0968 / (1.830 + 0.0968)$	5.03%
$\text{In Na}_2\text{CO}_3 = 100 - 5.03$	94.97%

a. Composition of original mixture:

Basis: 100 lb of products = 100 lb of original mixture.

Composition of basic quantity of products:

$\text{CaCO}_3 = 13.48/100 \text{ or}$	0.1348 lb-mol
$\text{CaO} = 0.21/56 \text{ or}$	0.00375 lb-mol
$\text{Na}_2\text{O} = 8.02/62 \text{ or}$	0.1293 lb-mol
$\text{Na}_2\text{CO}_3 = 0.61/106 \text{ or}$	0.00576 lb-mol

From the Na balance:

Total Na present = $(0.1293 + 0.00576)2$	0.270 lb-atom
Na originally in Na_2O = 0.270×0.0503	0.0136 lb-atom
Na originally in Na_2CO_3 = $0.270 - 0.0136$	0.256 lb-atom
Na_2O originally present = 0.0068 lb-mol or.....	0.42 lb
Na_2CO_3 originally present = 0.1282 lb-mol or....	13.60 lb

From the CO_2 balance:

Total CO_2 present = $0.1348 + 0.0058$	0.1406 lb-mol
CO_2 originally present in Na_2CO_3	0.1282 lb-mol
CO_2 originally present in CaCO_3	0.0124 lb-mol
CaCO_3 originally present = 0.0124 lb-mol or....	1.24 lb

From the Ca balance:

Total Ca present = $0.1348 + 0.00375$	0.1386 lb-atom
Ca originally in CaCO_3	0.0124 lb-atom
Ca originally in CaO	0.1262 lb-atom
CaO originally present = 0.1262 lb-mol or.....	7.07 lb

Water originally present.....	77.68 lb
Total weight of original materials (as verification).....	100.01 lb

CaCO_3	1.24%
CaO	7.07%
Na_2O	0.42%
Na_2CO_3	13.60%
H_2O	77.68%
	100.01%

b. Na_2CO_3 originally present.....	0.1282 lb-mol
CaO originally present.....	0.1262 lb-mol

Since 1.0 lb-mol of CaO combines with 1.0 lb-mol of Na_2CO_3 , the Na_2CO_3 is present in excess.

Percentage excess = $(0.1282 - 0.1262)/0.1262$	1.6%
Weight of limiting material (CaO) not converted....	0.21 lb

$$c. \text{ Degree of completion} = 100 - \frac{100 \times 0.21}{7.07} \dots\dots 97.03\%$$

Reaction Processes with Several Products. In most industrially important reaction processes not all the materials entering the reaction appear in a single product. For example, there may be an evolution of a gas or vapor from the reacting mass, as in the calcination of limestone, or there may be a separable residue which is removed from the major product, as when a precipitate is separated from a liquid product. In such cases it is of interest to calculate the weight and composition relationships of the reacting materials, the product, and the by-products. On the basis of the by-product these problems may be grouped into two general classes.

1. The by-products consist only of substances which were present in the original mass of reacting materials.
2. The by-products include some of the new products formed in the reaction.

These problems represent combinations of the type of problems of Chapter I with those already discussed in this chapter. Either class may be readily solved by considering the process to result from two separate successive steps. A process of the first class may be treated as consisting of, first, a separation of the by-products from the original reacting materials. Resulting from this separation will be a mass of the remaining reactants of hypothetical composition. The second step of the process is the reaction proper, into which it is considered that there enters only the group of reactants remaining after the separation involved in the first step. The first step of such a process involves a problem in change of weight and composition such as is discussed in Chapter I. After the composition of the remaining mass of reactants is calculated, the second step of the process may be treated exactly as the problems of the preceding section of this chapter.

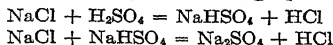
A process of the second class may be treated as consisting of a first step in which the reaction takes place and in which all the materials remain in a single product of a hypothetical weight and composition. In the second step of the process the by-products are considered as separating from this hypothetical product. The reaction of the first step is treated by the methods of the preceding section. The relationship between the weight and composition of the hypothetical single product and those of the actual products is determined by the methods of Chapter I.

In complicated cases both types of problems may be found combined in a single process. For example, in the combustion of coal some of the original reacting materials are lost through the grate into the ashes. The remaining materials react to form a stream of gases as the major product. From this stream of gases water vapor may be condensed changing the ultimate composition of the gaseous products. This process may be treated as occurring in three steps. First, is the separation, from the coal charged, of the materials lost with the ashes, leaving a material of hypothetical composition to actually enter the reaction. Second, is the reaction between the air and these remaining coal constituents to form a product in which all the entering materials appear. Third, is the separation of the water vapor which is condensed from this single product. By treating the steps as separate, successive problems such processes may be handled by the methods already described.

Problems of this, the most general, type may arise in almost innumerable forms and may be solved by dividing the process into separate steps

and treating each individually. The following illustration shows the method of procedure in a typical problem:

Illustration 6. The successive reactions in the manufacture of HCl from salt and sulphuric acid may be represented by the following equations:



In practice the salt is treated with aqueous sulphuric acid, containing 75% H_2SO_4 in slight excess of the quantity required to combine with all the salt to form Na_2SO_4 . Although the first reaction proceeds readily, strong heating is required for the second. In both steps of the process HCl and water vapor are evolved from the reaction mass.

"Salt cake" prepared by such a process was found to have the following composition:

Na_2SO_4	91.48%
NaHSO_4	4.79%
NaCl	1.98%
H_2O	1.35%
HCl.....	0.40%

a. Calculate the degree of completion of the first reaction and the degree of completion of the conversion to Na_2SO_4 of the salt charged.

b. Calculate the weight of salt cake formed per 1000 lb of salt charged.

c. Calculate the composition and weight of the gases removed during the process, per 1000 lb of NaCl charged.

Solution:

Basis of Calculation: 1000 lb of salt cake.

Composition:

$\text{Na}_2\text{SO}_4 = 914.8 \text{ lb or } 914.8/142.1$	6.44 lb-mols
$\text{NaHSO}_4 = 47.9 \text{ lb or } 47.9/120.1$	0.398 lb-mol
$\text{NaCl} = 19.8 \text{ lb or } 19.8/58.5$	0.338 lb-mol
H_2O	13.5 lb
HCl.....	4.0 lb

a. Since no H_2SO_4 is present in the product, the first reaction went to completion, all the sulphuric acid going to form bisulphate.

$$\text{Total Na present} = 2 \times 6.44 + 0.398 + 0.338 \dots\dots\dots 13.63 \text{ lb-atoms}$$

$$\text{Na present as } \text{Na}_2\text{SO}_4 = 2 \times 6.44 \dots\dots\dots 12.88 \text{ lb-atoms}$$

$$\text{Conversion of NaCl to } \text{Na}_2\text{SO}_4 = (12.88/13.63)100 \dots\dots\dots 94.4\%$$

b. Weight of NaCl equivalent to total Na in 1000 lb of salt cake = 13.63 lb-mols or 797 lb.

$$\text{Salt cake per 1000 lb of salt charged} = \frac{1000 \times 1000}{797} = 1257 \text{ lb}$$

c. From the information obtained in parts a and b together with that specified, the complete composition of the original reactants may be calculated. The degree of completion of the reaction is indicated by the composition of the salt cake. It is then possible to calculate the quantities of the various constituents present in the hypothetical material which would contain all the products of the reaction. The quantities of evolved gases can then be determined from the differences between the actual and the hypothetical product.

Basis of Calculation: 1000 lb of salt cake, formed from 797 lb or 13.63 lb-mols of NaCl.

H ₂ SO ₄ supplied = $6.44 + 0.398 = 6.84$ lb-mols or.....	671 lb
Aqueous acid supplied = $671/0.75$	895 lb
Water introduced = 895×0.25	224 lb
NaCl forming HCl = $13.63 - 0.338$	13.29 lb-mols
HCl formed = 13.29 lb-mols or.....	484 lb
HCl removed in process = $484 - 4$	480 lb
Water removed in process = $224 - 13.5$	209.5 lb
Total weight of gases removed = $480 + 210$	690 lb

Composition of gases by weight:

HCl.....	69.6%
H ₂ O.....	30.4%

Weight of water removed, per 1000 lb of NaCl charged =
 $(209.5/797) 1000$ 263 lb

Weight of HCl removed, per 1000 lb of NaCl charged =
 $(480/797) 1000$ 602 lb

Verification:

Basis: 1000 lb of salt cake.

Total weight of reactants = $797 + 895$	1692 lb
Total weight of products = $1000 + 690$	1690 lb

Reactions in Which Two or More Materials React Similarly. Many industrial charges contain mixtures of several compounds or elements capable of reacting in the same general way. For example, coal may contain carbon, hydrogen, and sulphur, all capable of oxidation. Dolomitic lime contains the oxides of calcium and magnesium, both of which react similarly in hydration and causticization. The presence of such a mixed charge adds but little complication to calculations of the types discussed in the preceding sections except as regards the extent to which the reactants enter into the reaction. If such a mixed reactant forms the limiting material which determines the possible extent of the reaction, the degree of completion may be expressed in two ways. First, the degree of completion of the reaction with each individual compound of the mixture may be separately expressed. Second, the overall degree of completion of the total reaction possible with the entire mixture of materials may be calculated. When it is required to calculate the composition of the products of the reaction of specified reactants it is necessary to specify individually the extent to which each component of a mixed reactant enters into the reaction, whether or not it is the limiting material.

Chemical Equivalents. In some problems it is not necessary that the detailed composition and weight of the products be calculated. In such cases it may be convenient to consider a mixed reactant, containing

several substances which react similarly, as though it were a single, hypothetical compound present in a quantity having a reacting value equivalent to the total of the compounds which are actually present.

The conventional expression of the "hardness" of a water in terms of calcium carbonate is an illustration of this method. The amount of calcium carbonate reported in a water analysis represents the quantity of this compound which contains an amount of calcium which is chemically equivalent to the total amount of alkaline earth and heavy metals actually present in the water. By determining the total chemical equivalent of a mixture of substances the quantity of materials required to react with it may be very easily calculated without further consideration of the individual components of the mixture. In many instances as in water-softening or in the production of metallurgical slags and glasses this method results in considerable simplification. For calculations of the amount of one compound chemically equivalent to another, the *chemical equivalent* may be conveniently used as the unit of quantity rather than simple weight units or molal quantities.

One gram-chemical-equivalent or *gram-equivalent* of a substance may be defined as the quantity which contains, will combine with, or is chemically equivalent to one gram-atom of active hydrogen. The *pound-equivalent* may be similarly defined as the quantity equivalent to one pound-atom of hydrogen. In dealing with mixed reacting materials the number of gram-equivalents of each constituent may be calculated and added together to obtain the total number of reacting equivalents present. This total number of reacting equivalents may be converted to the corresponding weight or number of mols of any desired single constituent which would have the same reacting value.

The determination of the weight of a gram-equivalent or pound-equivalent of any substance requires consideration of the composition of the substance and of the manner in which it may react.

Elements. Since hydrogen has a valence of 1, the weight of a gram-equivalent of an element will ordinarily be the weight of a gram-atom divided by the valence.

Acids. The weight of a gram-equivalent of an acid will be the number of grams of acid containing one gram-atom of ionizable hydrogen, or the weight of a gram-mol divided by the number of ionizable hydrogen atoms. In the case of an acid anhydride the weight of the gram-mol is divided by the number of atoms of ionizable hydrogen which would be present in the molecule were it normally hydrated. For example, SO_2 is the anhydride of H_2SO_3 , and the weight of one gram-equivalent is one-half the weight of the gram-mol.

Bases. Since one hydroxyl group is equivalent to one hydrogen atom

the weight of a gram-equivalent of a base is equal to the weight of the gram-mol, divided by the number of ionizable hydroxyl groups present. In the case of an anhydrous base, for example CaO , the weight of the gram-mol is divided by the number of hydroxyl groups present in the molecule when normally hydrated.

Salts. The weight of a gram-equivalent of a salt is generally equal to the weight of a gram-mol divided by the number of ionizable hydrogen atoms which were present in the acid from which the salt was formed.

Reducing Agents. The weight of one gram-equivalent of a reducing agent is equal to the weight of one gram-mol divided by the number of hydrogen atoms which may be supplied by one molecule or by twice the number of oxygen atoms which will combine with one molecule.

Oxidizing Agents. The weight of one gram-equivalent of an oxidizing agent is equal to the weight of one gram-mol, divided by the number of hydrogen atoms which may be oxidized by one molecule, or by twice the number of oxygen atoms which may be supplied by one molecule.

Ions. The weight of one gram-equivalent of an ion is equal to the weight of a gram-mol divided by the number of charges carried by the ion.

The advantage of the concept of the equivalent unit lies in the fact that one gram-equivalent of one material is chemically equivalent to or will react with exactly one gram-equivalent of any other material. The use of equivalent units is very valuable in volumetric quantitative analysis. A normal solution is one which contains one gram-equivalent of a reagent in one liter of solution at 20°C . Analytical calculations are greatly simplified by expressing all quantities in terms of equivalent units. A valuable method for the verification of the complete chemical analysis of inorganic salts is through calculation of the total reacting value of all the anions and then of all the cations present. These two reacting values must be equal. Such calculations are readily carried out by the use of equivalent units for the expression of quantities.

For industrial calculations the equivalent unit finds its principal application in certain problems dealing with mixtures of similarly reacting materials. *For all other calculations the use of the molal units is preferable.* The following illustrations demonstrate typical procedures for the advantageous use of equivalent units.

Illustration 7. The "temporary hardness" of a water represents the concentration of alkaline earth and heavy metals which are present in the form of bicarbonates. It is expressed in terms of the quantity of calcium carbonate which contains an amount of calcium equivalent to the metallic elements actually present. The temporary hardness is determined by titrating the water with a standard acid using methyl orange as the indicator.

A sample of 100 cc of water requires, for titration of its temporary hardness, 32.6 cc of sulphuric acid having a normality of 0.0193.

a. Calculate the temporary hardness of the water in milligrams of CaCO_3 per liter.

Solution:

Gram-equivalents of H_2SO_4 used in titration.....	(32.6/1000)0.0193
Gram-equivalents of bicarbonates in sample.....	(32.6/1000)0.0193
Gram-equivalents of calcium, equivalent to the bicarbonates.....	(32.6/1000)0.0193
Weight of 1 gram-equivalent of $\text{CaCO}_3 = 100/2$	50 grams
Milligrams of CaCO_3 equivalent to the bicarbonates in the sample = (32.6/1000)0.0193 \times 50 \times 1000....	31.4 mg
Temporary hardness = (31.4/100)1000.....	314 mg per liter

Illustration 8. In recovering the noble metal from defective miniature electric lamps the entire lamps and their bases are placed in a strong solution of hydrofluoric acid which dissolves all the material except the noble metals. The composition of the lamp is as follows:

SiO_2	61.82%
CaO	9.65%
Na_2O	13.46%
Cu	10.25%
Zn	4.38%
Au	0.29%
Pt	0.15%

Calculate the weight of HF required for the dissolution of 100 lb of the lamps.

Solution:

Basis: 100 lb of lamps.

In this case SiO_2 behaves as a base equivalent to 4 hydroxyl groups or 4 H atoms. The weight of 1 pound-equivalent is therefore one-fourth the molecular weight. Pound-equivalents present of the soluble substances:

$\text{SiO}_2 = 61.82 \div 60.1/4$	4.11 lb-equivalents
$\text{CaO} = 9.65 \div 56.1/2$	0.344 lb-equivalents
$\text{Na}_2\text{O} = 13.46 \div 62/2$	0.435 lb-equivalents
$\text{Cu} = 10.25 \div 63.6/2$	0.323 lb-equivalents
$\text{Zn} = 4.38 \div 65.4/2$	0.134 lb-equivalents
Total.....	5.346 lb-equivalents of acid-consuming materials
Acid required.....	5.346 lb-equivalents
1 lb-equivalent of HF weighs:.....	20 lb
Weight of HF required = 20 \times 5.346.....	107 lb

Illustration 9. A charge of iron ore and coke, prepared for a blast furnace, weighs 28,000 lb. It is found to contain 216 lb of CaO , 958 lb of Al_2O_3 , and 2038 lb of SiO_2 . It is desired to add enough limestone to the charge so that all silica may be fluxed to form silicates. Calculate the weight of calcium carbonate which is necessary assuming that only the monocalcium silicate is formed.

Solution: In this case silica acts as an acid, H_2SiO_3 , equivalent to 2 hydrogen atoms per molecule. The weight of 1 pound-equivalent is therefore equal to one-

half the molecular weight. Alumina acts as a base, equivalent to 6 hydroxyl groups.

Pound-equivalent present of reacting materials:

$\text{SiO}_2 = 2038 \div 60.1/2$	67.8 lb-equivalents
$\text{Al}_2\text{O}_3 = 958 \div 102/6$	56.4 lb-equivalents
$\text{CaO} = 216 \div 56/2$	7.7 lb-equivalents
Total basic materials = $56.4 + 7.7$	64.1 lb-equivalents
Excess of acid materials = $67.8 - 64.1$	3.7 lb-equivalents
Calcium carbonate required = 3.7 lb-equivalents or $3.7(100/2)$	185 lb

PROBLEMS

In order that any significant benefit may be derived from the solution of these problems the molar method of calculation must be used throughout.

Tables of common atomic weights and conversion factors will be found in the Appendix, pages 471-473.

1. In the manufacture of straw pulp for the production of a cheap straw-board paper, a certain amount of lime is carried into the beaters with the cooked pulp. It is proposed to neutralize this lime with commercial sulphuric acid, containing 77% H_2SO_4 by weight.

In a beater containing 2500 gal of pulp it is found that there is a lime concentration equivalent to 0.45 gram of CaO per liter.

- Calculate the number of pound-mols of lime present in the beater.
- Calculate the number of pound-mols and pounds of H_2SO_4 which must be added to the beater in order to provide an excess of 1.0% above that required to neutralize the lime.
- Calculate the weight of commercial acid which must be added to the beater for the conditions of b.
- Calculate the weight of calcium sulphate formed in the beater.

2. Phosphorus is prepared by heating, in the electric furnace, a thoroughly mixed mass of calcium phosphate, sand, and charcoal. It may be assumed that in a certain charge the following conditions exist: the amount of silica used is 10% in excess of that theoretically required to combine with the calcium to form the silicate; the charcoal is present in 40% excess of that required to combine, as carbon monoxide, with the oxygen which would accompany all the phosphorus as the pentoxide.

- Calculate the percentage composition of the original charge.
- Calculate the number of pounds of phosphorus obtained per 100 lb of charge, assuming that the decomposition of the phosphate by the silica is 90% complete and that the reduction of the liberated oxide of phosphorus, by the carbon, is 70% complete.

3. A coal containing 81% total carbon and 6% unoxidized hydrogen is burned in air.

- If air is used 30% in excess of that theoretically required, calculate the number of pounds of air used per pound of coal burned.
- Calculate the composition, by weight, of the gases leaving the furnace, assuming complete combustion.

4. In the Deacon process for the manufacture of chlorine, a dry mixture of hydrochloric acid gas and air is passed over a heated catalyst which promotes oxidation of the acid. Air is used in 30% excess of that theoretically required.

- Calculate the weight of air supplied per pound of acid.

- b. Calculate the composition, by weight, of the gas entering the reaction chamber.
 - c. Assuming that 60% of the acid is oxidized in the process, calculate the composition, by weight, of the gases leaving the chamber.
5. In order to obtain barium in a form which may be put into solution, the natural sulphate, barytes, is fused with sodium carbonate. A quantity of barytes, containing only pure barium sulphate and infusible matter, is fused with an excess of pure, anhydrous soda ash. Upon analysis of the fusion mass it is found to contain 11.3% barium sulphate, 27.7% sodium sulphate, and 20.35% sodium carbonate. The remainder was barium carbonate and infusible matter.
- a. Calculate the percentage completion of the conversion of the barium sulphate to the carbonate and the complete analysis of the fusion mass.
 - b. Calculate the composition of the original barytes.
 - c. Calculate the percentage excess in which the sodium carbonate was used above the amount theoretically required for reaction with all the barium sulphate.
6. In the manufacture of sulphuric acid by the contact process iron pyrites, FeS_2 , is burned in dry air, the iron being oxidized to Fe_2O_3 . The sulphur dioxide thus formed is further oxidized to the trioxide by conducting the gases mixed with air, over a catalytic mass of platinum-black at a suitable temperature. It will be assumed that in the operation sufficient air is supplied to the pyrites burner that the oxygen shall be 40% in excess of that required if all the sulphur actually burned were oxidized to the trioxide. Of the pyrites charged, 15% is lost by falling through the grate with the "cinder" and is not burned.
- a. Calculate the weight of air to be used per 100 lb of pyrites charged.
 - b. In the burner and a "contact shaft" connected with it, 40% of the sulphur burned is converted to the trioxide. Calculate the composition, by weight, of the gases leaving the contact shaft.
 - c. By means of the platinum catalytic mass, 96% of the sulphur dioxide remaining in the gases leaving the contact shaft is converted to the trioxide. Calculate the total weight of SO_3 formed per 100 lb of pyrites charged.
 - d. Assuming that all gases from the contact shaft were passed through the analyzer, calculate the composition by weight of the resulting gaseous products.
 - e. Calculate the overall degree of completion of the conversion of the sulphur in the pyrites charged to SO_3 in the final products.
7. In the LeBlanc soda process the first step is the preparation of "salt cake" according to the following reaction:



The acid used has a specific gravity of 58° Baumé, containing 74.4% H_2SO_4 . It is supplied in 2% excess of that theoretically required for the above reaction.

- a. Calculate the weight of acid supplied per 100 lb of salt charged.
 - b. Assume that the reaction goes to completion, all the acid forming bisulphate, and that in the process 85% of the HCl formed and 20% of the water present are removed. Calculate the weights of HCl and water removed per 100 lb of salt charged.
 - c. Assuming the conditions of part b, calculate the percentage composition of the remaining salt cake.
8. In the common process for the manufacture of nitric acid, sodium nitrate is treated with aqueous sulphuric acid containing 95% H_2SO_4 by weight. In order that

the resulting "niter cake," may be fluid it is desirable to use sufficient acid so that there will be 34% H_2SO_4 by weight, in the final cake. This excess H_2SO_4 will actually be in combination with the Na_2SO_4 in the cake, forming NaHSO_4 , although for purposes of calculation it may be considered as free acid. It may be assumed that the cake will contain 1.5% water, by weight, and that the reaction will go to completion, but that 2% of the HNO_3 formed will remain in the cake. Assume that the sodium nitrate used is dry and pure.

- a. Calculate the weight and percentage composition of the niter cake formed per 100 lb of sodium nitrate charged.
- b. Calculate the weight of aqueous acid to be used per 100 lb of sodium nitrate.
- c. Calculate the weights of nitric acid and water vapor distilled from the niter cake, per 100 lb of NaNO_3 charged.

9. Pure carbon dioxide may be prepared by treating limestone with aqueous sulphuric acid. The limestone used in such a process contained calcium carbonate and magnesium carbonate, the remainder being inert, insoluble materials. The acid used contained 12% H_2SO_4 by weight. The residue from the process had the following composition:

CaSO_4	8.56%
MgSO_4	5.23%
H_2SO_4	1.05%
Inerts.....	0.53%
CO_2	0.12%
Water.....	84.51%

During the process the mass was warmed and carbon dioxide and water vapor removed.

- a. Calculate the analysis of the limestone used.
- b. Calculate the percentage of excess acid used.
- c. Calculate the weight and analysis of the material distilled from the reaction mass per 1000 lb of limestone treated.

10. Barium carbonate is commercially important as a basis for the manufacture of other barium compounds. In its manufacture, barium sulphide is first prepared by heating the natural sulphate, barytes, with carbon. The barium sulphide is extracted from this mass with water and the solution treated with sodium carbonate to precipitate the carbonate of barium.

In the operation of such a process it is found that the solution of barium sulphide formed contains also some calcium sulphide, originating from impurities in the barytes. The solution is treated with sodium carbonate and the precipitated mass of calcium and barium carbonates is filtered off. It is found that 16.45 lb of dry precipitate are removed from each 100 lb of filtrate collected. The analysis of the precipitate is:

CaCO_3	9.9%
BaCO_3	90.1%

The analysis of the filtrate is found to be:

Na_2S	6.85%
Na_2CO_3	2.25%
H_2O	90.90%

The sodium carbonate for the precipitation was added in the form of anhydrous soda ash which contained calcium carbonate as an impurity.

- a. Determine the percentage excess sodium carbonate used above that required to precipitate the BaS and CaS.
 - b. Calculate the composition of the original solution of barium and calcium sulphides. (Note: Barium sulphide is actually decomposed in solution, existing as the compound $\text{OHBaSH} \cdot 5\text{H}_2\text{O}$. However, in this reaction the entire calculation may be carried out and compositions expressed as though the compound in solution were BaS.)
 - c. Calculate the composition of the dry soda ash used in the precipitation.
11. A mixture of 45% CaO, 20% MgO, and 35% NaOH by weight is used for treating ammonium carbonate liquor in order to liberate the ammonia.
- a. Calculate the number of pounds of CaO to which 1 lb of this mixture is equivalent.
 - b. Calculate the composition of the mixture, expressing the quantity of each component as the percentage it forms of the total reacting value of the whole.
 - c. Calculate the number of pounds of ammonia theoretically liberated by 1 lb of this mixture.
12. A water is found to contain the following metals, expressed in milligrams per liter: Ca, 32; Mg, 8.4; Fe (ferrous), 0.5.
- a. Calculate the "total hardness" of the water, expressed in milligrams of equivalent CaCO_3 per liter, the calcium of which would have the same reacting value as the total reacting value of the metals actually present.
 - b. Assuming that these metals are all combined as bicarbonates, calculate the cost of the lime required to soften 1000 gal of the water. Commercial lime, containing 95% CaO, costs \$8.50 per ton.
13. A glass for the manufacture of chemical ware is composed of the silicates and borates of several basic metals. Its composition is as follows:

SiO_2	66.2%	ZnO	10.3%
B_2O_3	8.2%	MgO	6.0%
Al_2O_3	1.1%	Na_2O	8.2%

Determine whether the acid or the basic constituents are in excess in this glass, and the percentage excess reacting value above that theoretically required for a neutral glass. (Assume that Al_2O_3 acts as a base and B_2O_3 as an acid, HBO_2 .)

CHAPTER III

IDEAL BEHAVIOR OF GASES

Solutions of scientific problems, in which energy changes are involved, are approached from two distinctly different viewpoints. From the *thermodynamic* standpoint all physical and chemical phenomena are considered only in terms of the final results which are produced or possible. No attention is given to the mechanism by which these effects are brought about. Scientific achievement, from the thermodynamic standpoint, lies in the development of mathematical relationships which express the changes accompanying natural processes. In order to further such development, abstract properties of matter such as entropy and fugacity are invented, mathematically defined, and assigned to substances, with no regard to their physical significances.

Diametrically opposed to the thermodynamic approach is that of *kinetic theory*. By means of the kinetic theory it is possible to present, often quantitatively, a mental picture of the actual mechanism of the energy changes in matter and to establish quantitative relationships. The results of intangible phenomena are explained in terms of the behavior of analogous mechanical systems of tangible natures. From such speculations have been developed very valuable physical and chemical concepts which may be expressed mathematically.

For the direct solution of many engineering and industrial problems involving energy changes the thermodynamic viewpoint is undeniably the more fruitful. However, the reasoning employed in the application of thermodynamic principles is organized and greatly clarified by a clear visualization of the mechanisms involved. Furthermore, many of the greatest of scientific discoveries have resulted from investigations which have been stimulated by the questions arising in extension of kinetic theories. It is of greatest value to develop complete and clear kinetic theory concepts of all natural phenomena, both as a means of organizing and clarifying reasoning and also of stimulating original thought and advance.

THE KINETIC THEORY OF GASES

As the basis of the kinetic theory it is assumed that all matter is composed of tiny particles which, by their behavior, determine its physical

and chemical properties. A gas is believed to be composed of molecules each of which is a material body and separate from all others. These particles are free to move about in space according to Newton's laws of the motion of material bodies. It is furthermore assumed that each particle behaves as a perfectly elastic sphere. As a consequence of this assumption there is no change in total kinetic energy or momentum when two particles collide or when a particle strikes an obstructing or confining surface. On the basis of these assumptions it is possible to explain many physical phenomena by considering that *each particle of matter is endowed with a certain inherent kinetic energy of translation*. As a result of this energy the particles will be in constant motion, striking against and rebounding from one another and from obstructing surfaces.

The energy which is represented by the sum of the energies of the component particles of matter is termed the total internal energy. When the heat content of a gas is increased, additional kinetic energy is imparted to the particles which compose it. The average quantity of kinetic energy of *translation* which is possessed by the particles of a gas determines the property known as *temperature*. At any specified temperature the particles of a gas possess definitely fixed, average kinetic energies of translation which may be varied only by a change in temperature resulting from the addition or removal of heat. Thus, an increase in temperature signifies an increase in average kinetic energy of translation which in turn is accompanied by increased speeds of translation of the particles. Conversely, when, by any means, the kinetic energies of translation of the particles of a gas are increased, the temperature is raised.

The theory outlined above accounts for the pressure which is exerted by a gas against the walls of a confining vessel. The translational motion of the particles is assumed to be perfectly random, in every direction, and it may be assumed for ordinary cases that the number of particles per unit volume will be constant throughout the space. These assumptions are justified when the number of particles per unit volume is very large, as it is when we deal with the gaseous state. Then, each element of area of confining surface will be subjected to continual bombardment by the particles adjacent to it. Each impact will be accompanied by an elastic rebound and will exert a pressure due to the change of momentum involved. In a pure, undissociated gas all particles may be considered to be of the same size and mass. On the basis of these assumptions an expression for pressure may be derived from the principles of mechanics.

In a cubical box, Fig. 1, each edge of which has a length l , are confined ν molecules of a pure gas. Each molecule has a mass m , and it is

assumed that all are in perfectly random, chaotic motion. For simplicity it will be assumed that all move at the mean speed u . Because of the perfectly random motion of the large number of particles under consideration it may be assumed that the situation is equivalent to that which would exist were one-third of the molecules moving parallel to the length of the box, one-third parallel to the depth and one-third parallel to the breadth. Under these conditions the top of the box would be subjected to bombardment by the molecules which are moving in a vertical direction. The other faces of the box would be similarly bombarded by equal numbers of molecules.

FIG. 1.

Each time that an upward-moving molecule strikes the top of the box with a velocity u it will rebound with a velocity u in the opposite direction. Such a collision will therefore result in a change of momentum equal to $2mu$. After rebounding from the top of the box the vertically moving molecule will traverse a distance l to the bottom, rebound from it, and again strike the top of the box after traveling a total distance equal to $2l$. Each vertically moving molecule will therefore strike the top of the box $u/2l$ times per second. Since one-third of the total number of molecules are moving vertically, there will be $vu/6l$ impacts of molecules against the top of the box, per second. These combined impacts will produce an average force F on the top of the box, equal to the total rate of change of momentum.

Then

$$F = 2mu \times \frac{vu}{2l} = \frac{1}{2} \frac{mvu^2}{l} \quad (1)$$

This force F is distributed uniformly over the top of the box and therefore corresponds to a pressure p per unit area.

$$p = \frac{1}{3} \frac{mvu^2}{l} \times \frac{1}{l^2} = \frac{1}{3} \frac{mvu^2}{V} \quad (2)$$

where

$$V = l^3 = \text{the volume of the box}$$

An equal pressure will be exerted against each of the other faces of the box.

The term mu^2 represents twice the kinetic energy of translation of each of the molecules. Then

$$2 \times \frac{1}{2} mvu^2 = 2E \quad (3)$$

where

E = mean translational kinetic energy per molecule

From the definition of the molal units of quantity it was pointed out that one mol of a substance will contain a definite number of single molecules, the same for all substances. Then

$$\nu = nN \quad (4)$$

where

n = number of mols in volume V

N = number of molecules in a mol, a universal constant equal to 6.06×10^{23} for the gram-mol

Combining (3) and (4),

$$pV = n\frac{1}{3}Nmu^2 = n\frac{2}{3}NE \quad (5)$$

where NE represents the total translational kinetic energy possessed by one mol of gas.

From extensive experimental investigations the simple gas law has been empirically developed. In fact, the definition of temperature is based on this relationship.

$$pv = RT \quad (6)$$

or

$$pV = nRT \quad (7)$$

where

R = a proportionality factor

T = absolute temperature

v = volume of one mol of gas

n = number of mols of gas

V = volume of n mols of gas

Rearranging (6)

(8)

Assuming the validity of the Avogadro principle that equimolal quantities of all gases occupy the same volume at the same conditions of temperature and pressure, it follows from Equation (8) that the gas law factor R is a universal constant. The Avogadro principle and the simple gas law have been experimentally shown to approach perfect validity for all gases under conditions of extreme rarefaction, that is, where the number of molecules per unit volume is very small. The constant R may be evaluated from a single measurement of the volume occupied by a known molal quantity of any gas at a known temperature and at a known reduced pressure.

Combining Equations (5) and (7):

$$= RT \quad (9)$$

or

Equation (9) states that the average kinetic energy of translation of a molecule in the gaseous state is directly proportional to the absolute temperature. The absolute zero is the temperature at which the kinetic energies of all molecules become zero and molecular motion ceases. From the fact that R , the gas law constant, and N , the Avogadro number, are universal constants, it follows that Equation (9) must apply to all gases. In other words, *the average translational kinetic energy with which a gas molecule is endowed is dependent only upon the absolute temperature and is independent of its nature and size.* This conclusion is of far-reaching significance. It follows that a molecule of hydrogen possesses the same average translational kinetic energy as does a molecule of bromine at the same temperature. Since the bromine molecule has eighty times the mass of the hydrogen molecule the latter must move at a correspondingly higher velocity of translation. If the temperature increases, the squares of the velocities of translation of both molecules will be increased in the same proportion.

From the theory outlined in the preceding paragraphs it is possible to form a definite mental picture of the mechanical nature of a gas. The actual component parts of the gas are invisible and of an abstract and rather theoretical nature. The kinetic theory merely presents a mechanical analogy by which the phenomena of the gaseous state are explained in terms of the familiar laws of energy and of the behavior of particles of rigid matter of tangible dimensions. The analogy calls to mind a box in which are contained energized, elastic marbles which are in constant motion, colliding with one another and with the confining walls. An increase in temperature merely signifies an increased velocity of motion of each marble. A clear mental picture of such an analogy is of great value in fully understanding the properties of matter and in making use intelligently of thermodynamic relationships.

The derivation of Equation (2) which is employed above is based on several assumptions which are known to be incorrect. It is well known that not all molecules of a substance move at the same speed when at the same temperature. The actual speeds vary above and below the average according to a definite law of distribution. It was also assumed that each molecule moves back and forth across the confining space without contact with other molecules. Actually an average molecule may move only a very short distance, known as the *mean free path*, before it strikes another molecule and changes its direction. A rigorous derivation which takes these facts into account is of very tedious form but has been successfully carried out. The result is exactly the same as that derived above, indicating that the simplifying assumptions are justified.

Extension of the Kinetic Theory. Although the kinetic theory was originally developed to explain the behavior of gases, it has been extended and found to apply with good approximation wherever small particles of matter are permitted to move freely in space. It has been shown that all such particles *may be considered as endowed with the same kinetic energy of translation when at the same temperature regardless of composition or size.* This principle is believed to apply not only to the molecules of all gases but also to the molecules of all liquids and of substances which are dissolved in liquids. It has been extended still further and shown to apply also to particles of solid matter of considerable size suspended in gases or liquids. Thus, at any selected temperature, a molecule of hydrogen gas, a molecule of iodine vapor, a molecule of liquid water, and a molecule of liquid mercury all are supposed to possess the same translational kinetic energy, indicated by Equation (5). Furthermore, this same energy is possessed by a molecule of sulphuric acid in solution in water and by each of the ions formed by the dissociation of such a molecule. A colloidal particle of gold, containing hundreds of atoms, or a speck of dust suspended in air, each presumably has the same translational kinetic energy as does a molecule of hydrogen gas at the same temperature. The larger particles must therefore exhibit correspondingly slower velocities of translational motion. This generalization is of the greatest importance in the explanation of such phenomena as diffusion, heat conduction, osmotic pressure, and the general behavior of colloidal systems.

The Gas Law Units and Constants. In the use of the gas law equations great care must be exercised that consistent units are employed for the expression of both the variable and constant terms. Temperature must always be expressed on an absolute scale. Two such scales are in common use. The Kelvin scale corresponds, in the size of its unit degree, to the Centigrade scale. The zero of the Centigrade scale corresponds to 273.1 degrees on the Kelvin scale. Thus:

$$X^{\circ} \text{C} = (X + 273.1)^{\circ} \text{K (Kelvin)}$$

The Rankine scale of absolute temperature corresponds, in the size of its unit degree, to the Fahrenheit scale. The zero of the Fahrenheit scale corresponds to 460 degrees on the Rankine scale. Thus:

$$X^{\circ} \text{F} = (X + 460)^{\circ} \text{R (Rankine)}$$

The Avogadro number N denoting the number of molecules in a mol is one of the most important of physical constants and has been carefully determined by a variety of methods. The accepted value is 6.06×10^{23}

for the number of molecules in one gram-mol, or 2.75×10^{26} molecules per pound-mol.

Equation (10) may be solved for the gas constant R :

$$R = \frac{2}{3} \frac{NE}{T} \quad (11)$$

From Equation (11) it is seen that R represents two-thirds of the translational kinetic energy possessed by one mol per degree of absolute temperature. The numerical value of R has been carefully determined and may be expressed in any desired energy units. Following are values corresponding to various systems of units.

UNITS OF PRESSURE	UNITS OF VOLUME	R
<i>Per gram-mol</i> (temperatures: Kelvin)		
Atmospheres	Cubic centimeters	82.06
<i>Per pound-mol</i> (temperatures: Rankine)		
Pounds per square inch	Cubic inches	18,510
Pounds per square inch	Cubic feet	10.71
Atmospheres	Cubic feet	0.729

APPLICATIONS OF THE SIMPLE GAS LAW

When substances exist in the gaseous state two general types of problems arise in determining the relationships between weight, pressure, temperature, and volume. The first type is that in which are involved only the last three variables—pressure, temperature, and volume. For example, a specified volume of gas is initially at a specified temperature and pressure. The conditions are changed, two of the variables in the final state being specified, and it is desired to calculate the third. For such calculations it is not required to know the weight of the gas. The second, more general type of problem involves the weight of the gas. A specified weight of substance exists in the gaseous state under conditions, two of which are specified and the third is to be calculated. Or, conversely, it is desired to calculate the weight of a given quantity of gas existing at specified conditions of temperature, pressure, and volume.

Problems of the first type, in which weights are not involved, may be readily solved by means of the proportionality indicated by the gas law. Equation (7) may be applied to n mols of gas at conditions p_1 , V_1 , T_1 and also at conditions p_2 , V_2 , T_2 .

$$p_1 V_1 = nRT_1$$

$$p_2 V_2 = nRT_2$$

Combining:

$$n \cdot V = \frac{T_1}{T_2} \quad (12)$$

This equation may be applied directly to any quantity of gas. If the three conditions of state 1 are known, any one of those of state 2 may be calculated to correspond to specified values of the other two. Any units of pressure, volume, or absolute temperature may be used, the only requirement being that the units in both initial and final states be the same.

Equation (7) is in form to permit direct solution of problems of the second type in which are involved both weights and volumes of gases. With weights expressed in molal units the equation may be solved for any one of the four variables if the other three are known. However, this calculation requires a value of the constant R expressed in units to correspond to those used in expressing the four variable quantities. So many units of expression are in common use for each variable quantity that a very large table of values of R would be required or else the variable quantities would have to be converted into standard units. Either method is inconvenient.

It proves much more desirable to separate such calculations into two steps. As a primary constant, the *normal molal volume* is used instead of R . The normal molal volume is the volume occupied by one mol of a gas at arbitrarily selected *standard conditions*, assuming that the simple gas law is obeyed. The normal molal volume at any one set of standard conditions must, assuming the validity of Equation (7), be a universal constant, the same for all gases. The volume, at the standard conditions, of any weight of gas is the product of the number of mols present and the normal molal volume. The general type of problem involving weights and volumes at any desired conditions may then be solved in two steps. In one, the differences between the properties of the gas at standard conditions and at those specified in the problem are determined by Equation (12). In the other step the relationship between volume at standard conditions and weight is determined by means of the normal molal volume constant.

Standard Conditions. An arbitrarily specified standard state of temperature and pressure serves two purposes. It establishes the normal molal volume constant required in the system of calculation described in the preceding section. It also furnishes convenient specifications under which quantities of gases may be compared when expressed in terms of volumes. Some such specification is necessary because of the fact that the volume of a gas depends not only on the quantity but on the temperature and pressure as well.

Several specifications of standard conditions are in more or less common use but the one most universally adopted is that of a temperature of 0°C and a pressure of one atmosphere. It is recommended that these conditions be adopted as the standard for all calculations. Under these

conditions the normal molal volumes are as follows (the abbreviation S.C. is used to designate the standard conditions):

Volume of 1 gram-mol S.C.	= 22.41 liters
Volume of 1 pound-mol S.C.	= 359 cubic feet

These important constants should be memorized. The conditions of the standard state may be expressed in any desired units as in the following table:

STANDARD CONDITIONS

<i>Temperature</i>	<i>Pressure</i>
0° Centigrade	1 atmosphere
273° Kelvin	760 mm of mercury
32° Fahrenheit	29.92 in. of mercury
492° Rankine	14.70 lb per sq in.

There are many substances which cannot actually exist in the gaseous state at these specified conditions. For example, at a temperature of 0° C water cannot exist in a stable gaseous form at a pressure greater than 4.6 mm of mercury. Higher pressures cause condensation. Yet, it is convenient to refer to the hypothetical volume occupied by water vapor at standard conditions. In such a case the volume at standard conditions indicates the hypothetical volume which would be occupied by the substance if it could exist in the vapor state at these conditions assuming that it obeyed the simple gas law. It is perfectly legitimate to use such hypothetical volumes for purposes of calculation.

Gauge Pressure. All ordinary pressure gauges indicate the magnitude of pressure above or below that of the atmosphere. In order to obtain the *absolute pressure* which must be used in the gas laws, the pressure of the atmosphere must be added to the *gauge pressure*. Where the atmospheric pressure is not known, the normal value of 14.7 pounds per square inch or 29.92 inches of mercury is assumed.

Gas Densities and Specific Gravities. The density of a gas is ordinarily expressed as the weight in grams of one liter or the weight in pounds of one cubic foot. Unless otherwise specified the volumes are at the standard conditions of 0° C and a pressure of 1.0 atmosphere. On this basis air has a normal density of 1.293 grams per liter or of 0.0807 pound per cubic foot.

The *specific gravity* of a gas is usually defined as the ratio of its density to that of air at the same conditions of temperature and pressure.

Calculations. The gas law expresses the relationship between four properties of a gas: mass, volume, pressure, and temperature. In order to calculate any one of these properties the others must be known or

specified. Four different types of problems arise, classified according to the property being sought. The following illustrations show the application of the recommended method of calculation to each of these types of problems.

For establishment of correct ratios to account for the effects of pressure and temperature a simple rule may be followed which offers less opportunity for error than attempting to recall Equation (12). The ratios of pressures or temperatures should be greater than unity when the changes in pressure or temperature are such as to cause increase in volume. The ratios should be less than unity when the changes are such as to cause decrease in volume.

Illustration 1 (Volume Unknown). Calculate the volume occupied by 30 lb of chlorine at a pressure 743 mm of Hg and 70° F.

Basis: 30 lb of chlorine or $30/71 = 0.423$ lb-mol.

Volume at S.C. = $0.423 \times 359 = 152$ cu ft.

70° F = 530° Rankine.

Volume at 743 mm Hg, 70° F = $152 \times \frac{760}{743} \times \frac{530}{492} = 167$ cu ft.

Illustration 2 (Weight Unknown). Calculate the weight of 100 cu ft of water vapor, measured at a pressure of 15.5 mm of Hg and 23° C.

Basis: 100 cu ft of water vapor at 15.5 mm Hg, 23° C.

Volume at S.C. $\propto \sqrt{\frac{760}{15.5}} \wedge \frac{296}{298} = 1.88$ cu ft.

Mols of H₂O = $1.88 \div 359 = 0.00523$ lb-mol.

Weight of H₂O = $0.00523 \times 18 = 0.0942$ lb.

Illustration 3 (Pressure Unknown). It is desired to compress 10 lb of carbon dioxide to a volume of 20 cu ft. Calculate the pressure in pounds per square inch which is required at a temperature of 30° C assuming the applicability of the simple gas law.

Basis: 10 lb of CO₂ or $10/44 = 0.228$ lb-mol.

Volume at S.C. = $0.228 \times 359 = 81.7$ cu ft.

From Equation (12):

$$P_1 \frac{V_1}{T_1} = P_2 \frac{V_2}{T_2}$$

30° C = 303° K.

Pressure at 20 cu ft, 30° C = $14.7 \frac{81.7}{20} \times \frac{303}{273} = 66.6$ lb sq in.

Illustration 4 (Temperature Unknown). Assuming the applicability of the simple gas law, calculate the maximum temperature to which 10 lb of nitrogen, enclosed in a 30 cu ft chamber, may be heated without the pressure exceeding 150 lb sq in.

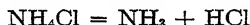
Basis: 10 lb of nitrogen or $10/28 = 0.357$ lb-mol.

Volume at S.C. = $0.357 \times 359 = 128.1$ cu ft.

Temperature at 30 cu ft, 150 lb/sq in. =

$$273 \frac{150}{14.7} \times \frac{30}{128.1} = 652^\circ \text{K or } 379^\circ \text{C}$$

Dissociating Gases. Certain chemical compounds when in the gaseous state apparently do not even approximately follow the relationships deduced above. Ammonium chloride, nitrogen peroxide, and phosphorus pentachloride exhibit this apparent abnormality. It has been definitely proved that these abnormalities result from dissociation of the molecules into equilibrium mixtures containing two or more other compounds. Ammonium chloride molecules in the vapor state separate into molecules of hydrogen chloride and ammonia:



Thus gaseous ammonium chloride is not a pure gas but a mixture of three gases, NH_4Cl , HCl , and NH_3 . By decomposition two gas particles are produced from one, and the pressure or volume of the gas increases above that which would exist had no decomposition taken place. For this reason, when one gram-mol of ammonium chloride is vaporized the volume occupied will be much greater than that indicated by Equation (7), page 39. However, when proper account is taken of the fact that in the gaseous state there is actually more than one gram-mol present, it is found that the gas laws apply. Conversely, from the apparent deviation from the gas laws the percentage of dissociation can be calculated if the chemical reaction involved is known.

Illustration 5. When heated to 100°C and 720 mm pressure 17.2 grams of N_2O_4 gas occupy a volume of 11,450 cc. Assuming that the ideal gas law applies, calculate the percentage dissociation of N_2O_4 to NO_2 .

$$\text{Gram-mols of } \text{N}_2\text{O}_4 \text{ initially present} = \frac{17.2}{92} = 0.187$$

Let x = gram-mols of N_2O_4 dissociated. Then $2x$ = gram-mols of NO_2 formed.

Total gram-mols present after dissociation =

$$0.187 - x + 2x = \frac{11,450}{22,400} \times \frac{273}{373} \times \frac{720}{760} = 0.355$$

Solving, $x = 0.168$.

$$\text{Percentage dissociation} = \frac{0.168}{0.187} \times 100 = 90\%$$

GASEOUS MIXTURES

In a homogeneous mixture of different gases the molecules of each component gas are uniformly distributed throughout the entire volume of the containing vessel and the molecules of each component gas contribute by their impacts to the total pressure exerted by the entire mixture. The total pressure is equal to the sum of the pressures exerted by the molecules of each component gas. These statements apply to all gases, whether or not their behavior is ideal. In a mixture of ideal gases the molecules of each component gas behave independently as though they alone were present in the container. Before considering the actual behavior of gaseous mixtures it will be necessary to define two terms commonly employed, namely, partial pressure and partial volume. By definition, the *partial pressure of a component gas which is present in a mixture of gases is the pressure that would be exerted by that component gas if it alone were present in the same volume and at the same temperature as the mixture.* By definition, the *partial volume of a component gas which is present in a mixture of gases is the volume that would be occupied by that component gas if it alone were present at the same pressure and temperature as the mixture.*

The partial pressure as defined above does not represent the actual pressure exerted by the molecules of the component gas when present in the mixture except under certain limiting conditions. Also, the partial volume does not represent the volume occupied by the molecules of the component gas when present in the mixture, for obviously the molecules are distributed uniformly throughout the volume of the mixture.

From the simple kinetic theory of the constitution of gases it would be expected that many properties of gaseous mixtures would be additive. The additive nature of partial pressures is expressed by *Dalton's law*, which states that *the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures*, that is:

$$p = p_A + p_B + p_C + \cdots \quad (13)$$

where p is the total pressure of the mixture and p_A , p_B , p_C , etc., are the partial pressures of the component gases as defined above.

Similarly, the additive nature of partial volumes is given by the *law of Amagat*, also called *Leduc's law*, which states that *the total volume occupied by a gaseous mixture is equal to the sum of the partial volumes*, that is:

$$V = V_A + V_B + V_C + \cdots \quad (14)$$

where V is the total volume of the mixture and V_A , V_B , V_C , etc., are the

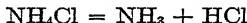
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IDEAL BEHAVIOR OF GASES

partial volumes of the component gases as defined above. It will be shown later that each of these laws is correct where conditions are such that the mixture and each of the components obey the ideal gas law.

Where small molal volumes are encountered, such that the simple gas law does not apply, the two statements are incompatible and neither is rigorously correct. Under such conditions pressures may not be additive, because the introduction of additional molecules into a gas-filled container may appreciably affect the pressure exerted by those already there. The presence of new molecules will reduce the space available for the free motion of those originally present and will exert attractive forces on them. Similarly, if quantities of two gases at the same pressure are allowed to mix at that same pressure, the like molecules of each gas will be separated by greater distances and will be in the presence of unlike molecules, which may alter the order of attractive forces existing between them. As a result, the volume of the mixture may be quite different from the sum of the original volumes. These same effects are present but negligible under the conditions of large molal volumes and wide separation of molecules.

Where conditions are such that the ideal gas law is applicable:

(15)

where V = total volume of mixture
 n_A = number of mols of component A in mixture.

Similar equations represent the partial pressures of components B , C , etc. Combining these equations with Dalton's law, Equation (13):

$$p = n_B \cdot c + \dots \cdot \frac{RT}{V} \quad (16)$$

This equation relates the pressure, temperature, volume, and molal quantity of any gaseous mixture under such conditions that the mixture and each of the components follow the simple gas law and Dalton's law.

By combining Equations (15) and (16) a useful relationship between total and partial pressure is obtained.

$$p_A = \frac{n_A}{n_A + n_B + n_C + \dots} p \quad (17)$$

The quantity $n_A/(n_A + n_B + n_C + \dots)$ is termed the mol fraction of component A . Obviously, the sum of the mol fractions of all the components of a mixture must equal unity. The mol fraction multiplied by 100 is termed the mol percentage. Mol fractions or mol percentages provide a very convenient method for the expression of the analyses of

mixtures or solutions. Equation (17) then signifies that, *where the simple gas law may be applied, the partial pressure of a component of a mixture is equal to the product of the total pressure and the mol fraction of that component.*

Where conditions are such that the ideal gas law is applicable

$$pV_A = n_A RT \quad (18)$$

$$pV_B = n_B RT \quad (19)$$

where V_A , V_B , etc., are the partial volumes as defined above.

Adding these equations,

$$p(V_A + V_B + \dots) = (n_A + n_B + \dots) RT \quad (20)$$

Combining Equations (18) and (19) with Amagat's law (Equation 14),

$$\frac{V_A}{V} = \frac{n_A}{n}$$

or

$$V_A = N_A V \quad (22)$$

where

N_A is the mol fraction of component A

Equation (22) signifies that, *where the simple gas law may be applied, the partial volume of a component of a gaseous mixture is equal to the product of the total volume and the mol fraction of that component.*

From Equations (16) and (20) it is evident that when the ideal gas law is valid both Amagat's and Dalton's law apply, that is, both partial volumes and partial pressures are additive.

Composition by Volume. The percentage by volume of a component in a gaseous mixture is ordinarily understood to be the experimental result obtained in gas analysis where each component gas is removed one at a time and the volume of the remaining mixture always measured at the same total pressure. The shrinkage in volume as each component is removed expressed as a percentage of the original volume represents the volume percentage composition.

The volume percentage composition obtained corresponds to the ratio of partial volume to total volume when Amagat's law applies and corresponds to the mol fraction in percentage where the ideal gas law applies.

It is frequently necessary to convert gas analyses from the volume to the weight basis, and the reverse. This conversion is readily carried out if the simple gas or Amagat's law is applicable.

If it is desired to convert a composition from a volume to a weight basis it is best to select as a basis of calculation a unit molal quantity of the mixture. The molal quantities of the various components are

then represented by their percentages by volume. The quantity of each component is then converted into weight units and the total weight of the basic quantity of mixture determined. From this information the percentage composition by weight is directly calculated.

Illustration 6. A mixture of gases has the following composition by volume:

O ₂	6.3%
SO ₂	14.6%
N ₂	79.1%
	<hr/>
	100.0%

Assuming the applicability of the simple gas law, calculate the percentage composition by weight of this mixture.

Basis: 1 lb-mol of the mixture.

O ₂ = 0.063 lb-mol or.....	2.02 lb
SO ₂ = 0.146 lb-mol or.....	9.36 lb
N ₂ = 0.791 lb-mol or.....	22.18 lb
	<hr/>
Total weight.....	33.56 lb

Composition by weight:

O ₂ = 2.02/33.56.....	6.0%
SO ₂ = 9.36/33.56.....	27.9%
N ₂ = 22.18/33.56.....	66.1%
	<hr/>
	100.0%

Where it is desired to convert an analysis from a weight to a volume basis the reverse procedure is followed. A unit weight of the mixture is adopted as the basis of calculation, and the quantity present of each component is converted to molal units. The total number of mols present is thus determined, and from it the mol percentages or volume percentages of the components are calculated.

Illustration 7. A mixture of ammonia and air has the following percentage composition by weight:

O ₂	21.1%
N ₂	69.8%
NH ₃	9.1%
	<hr/>
	100.0%

Calculate the percentage composition by volume of this mixture, assuming the applicability of the simple gas law.

Basis: 100 grams of the mixture.

O ₂ = 21.1 grams or.....	0.659 gram-mol
N ₂ = 69.8 grams or.....	2.495 gram-mols
NH ₃ = 9.1 grams or.....	0.535 gram-mol
	<hr/>
Total.....	3.689 gram-mols

Molal composition = volume composition:

O ₂	= 0.659/3.689	17.9%
N ₂	= 2.495/3.689	67.6%
NH ₃	= 0.535/3.689	14.5%
		100.0%

Average Molecular Weight of a Gaseous Mixture. A certain group of components of a mixture of gases may in many cases pass through a process without being changed in composition or weight. For example, in a drying process, dry air merely serves as a carrier for the vapor being removed and undergoes no change in composition or in weight. It is frequently convenient to treat such a mixture as though it were a single gas and assign to it an average molecular weight which may be used for calculation of its weight and volume relationships. Such an average molecular weight has no physical significance from the standpoint of the molecular theory and is of no value if any component of the mixture takes part in a reaction or is altered in relative quantity. The average molecular weight is calculated by adopting a unit molal quantity of the mixture as the basis of calculation. The weight of this molal quantity is then calculated and will represent the average molecular weight. By this method the average molecular weight of air is found to be 29.0.

Illustration 8. Calculate the average molecular weight of a flue gas having the following composition by volume:

CO ₂	13.1%
O ₂	7.7%
N ₂	79.2%
	<hr/> 100.0%

Basis: 1 gram-mol of the mixture,

CO ₂ = 0.131 gram-mol or	5.76 grams
O ₂ = 0.077 gram-mol or	2.46 grams
N ₂ = 0.792 gram-mol or	22.18 grams

Weight of 1 gram-mol = 30.40 grams, which is equal to the average molecular weight.

Densities of Gaseous Mixtures. If the composition of a gas mixture is expressed in molal or weight units the density is readily determined by selecting a unit molal quantity or weight as the basis and calculating its volume at the specified conditions of temperature and pressure. This method may be applied to mixtures which do or do not follow the simple gas law. Where the simple gas law is applicable, a more direct method is first to obtain the volume of the basic quantity of mixture at standard conditions by multiplying the number of mols by the normal

molal volume. The volume at the specified conditions is then calculated from the simple gas law proportion.

Illustration 9. Calculate the density in pounds per cubic foot at 29 in. of Hg and 30° C of a mixture of hydrogen and oxygen which contains 11.1% H₂ by weight.

Basis: 1 lb of mixture.

H ₂ = 0.111 lb or.....	0.0555 lb-mol
O ₂ = 0.889 lb or.....	0.0273 lb-mol
Total molal quantity.....	0.0833 lb-mol
Volume at S.C. = 0.0833 × 359.....	29.9 cu ft
Volume at 29 in. Hg, 30° C = 29.9 × $\frac{29.92 \times 303}{29.0 \times 273}$	34.2 cu ft
Density at 29 in. Hg, 30° C = $\frac{1}{34.2}$	0.0292 lb cu ft

If the composition of a mixture of gases is expressed in volume units, the simple gas law is ordinarily applicable. In this case the volume analysis is the same as the molal analysis, and the density is readily calculated on the basis of a unit molal quantity of the mixture. The weight of the basic quantity is first calculated and then its volume at the specified conditions.

Illustration 10. Air is assumed to contain 79.0% nitrogen and 21.0% oxygen by volume. Calculate its density in grams per liter at a temperature of 70° F and a pressure of 741 mm of Hg.

Basis: 1.0 gram-mol of air.

O ₂ = 0.210 gram-mol or.....	6.72 grams
N ₂ = 0.790 gram-mol or.....	22.10 grams
Total weight.....	28.82 grams
Volume at S.C.....	22.41 liters
Volume, 741 mm Hg, 70° F = 22.41 × $\frac{760 \times 530}{741 \times 492}$	24.8 liters
Density = $\frac{28.82}{24.8}$ = 1.162 grams per liter (741 mm Hg, 70° F)	

The actual density of the atmosphere is slightly higher owing to the presence of about 1 per cent of argon which is classed as nitrogen in the above problem. The mixture of nitrogen and inert gases in the atmosphere may be termed *atmospheric nitrogen*. The average molecular weight of this mixture is 28.2.

VOLUME CHANGES WITH CHANGE IN COMPOSITION

Such industrial processes as gas absorption, drying, and some types of evaporation involve changes in the compositions of gaseous mixtures due to the addition or removal of certain components. In a drying process, water vapor is added to a stream of air. In the scrubbing of coal gas, ammonia is removed from the mixture. It is of interest to

calculate the relationships existing between the initial and final volumes of the mixture and the volume of the material removed or added to the mixture in such a process. The situation is ordinarily complicated by changes of temperature and pressure concurrent with the composition changes. It is evident that these problems are of the same type as those discussed in Chapter I with the added complication that the relationships between weights and volumes are involved. Solution may be carried out by the methods of Chapter I if the quantities specified in the problem are first converted to weight or molal units. The quantities which are unknown may then be calculated in these same units. The last step will then be the conversion of the results from molal or weight units into volumes at the specified conditions of temperature and pressure. The relationships between molal units and volumes under any conditions are expressed by Equations (16) to (22). This method of solution may be applied with the use of either the simple gas law or the more accurate equations. The following illustration demonstrates the method for a case in which the simple gas law is applicable. The same procedure is followed as would be necessary were one of the other equations used. As in the problems of Chapter I, the calculations must be based on a definite quantity of a component which passes through the process unchanged.

✓ **Illustration 11.** Combustion gases having the following molal composition are passed into an evaporator at a temperature of 200° C and a pressure of 743 mm of Hg.

Nitrogen.....	79.2%
Oxygen.....	7.2%
Carbon dioxide.....	13.6%
	<hr/> 100.0%

Water is evaporated, the gases leaving at a temperature of 85° C and a pressure of 740 mm of Hg with the following molal composition:

Nitrogen.....	48.3%
Oxygen.....	4.4%
Carbon dioxide.....	8.3%
Water.....	39.0%
	<hr/> 100.0%

- Calculate the volume of gases leaving the evaporator per 100 cu ft entering.
- Calculate the weight of water evaporated per 100 cu ft of gas entering.

Solution:

Basis: 1 gram-mol of the entering gas.

N ₂	0.792 gram-mol
O ₂	0.072 gram-mol
CO ₂	0.136 gram-mol

Total volume (743 mm Hg, 200° C) calculated from Equations (14) and (20):

$$p = 743/760 \text{ or } 0.978 \text{ atm}$$

$$T = 473^\circ \text{ K}$$

$$R = 82.1 \text{ cc atm per } ^\circ \text{K}$$

$$V = \frac{(n_A + n_B + n_C) RT}{p} = \frac{(0.792 + 0.072 + 0.136) 82.1 \times 473}{0.978}$$

$$\frac{473}{0.978} = 39,750 \text{ cc or } 1.40 \text{ cu ft}$$

(743 mm Hg, 200° C)

~~1.0~~ ^{3 gm-mol}

This 1.0 ~~lb-mol~~ of gas entering forms 61% by volume of the gases leaving the evaporator.

$$\text{Gases leaving} = \frac{1.0}{0.61} = 1.64 \text{ gram-mols.}$$

$$\text{Water leaving} = 1.64 - 1.0 = 0.64 \text{ gram-mol.}$$

Volume of gas leaving, from Equations (14) and (20):

$$p = 740/760 = 0.973 \text{ atm}$$

$$T = 358^\circ \text{ K}$$

$$R = 82.1 \text{ cc atm per } ^\circ \text{K}$$

$$V = \frac{(0.792 + 0.072 + 0.136 + 0.64) \times 82.1 \times 358}{0.973}$$

$$\frac{1.64 \times 82.1 \times 358}{0.973} = 49,500 \text{ cc or } \dots\dots\dots 1.75 \text{ cu ft}$$

Volume of gas leaving per 100 cu ft entering,

$$\frac{1.75 \times 100}{1.40} \dots\dots\dots 125 \text{ cu ft (740 mm Hg, } 85^\circ \text{ C)}$$

$$\text{Weight of water leaving evaporator} = 0.64 \times 18 = 11.5 \text{ grams or } 0.0254 \text{ lb}$$

Weight of water evaporated per 100 cu ft of gas entering,

$$0.0254 \times 100$$

$$1.40$$

$$1.81 \text{ lb}$$

Partial Volume Method. Where the simple gas law may be applied, the method of calculation demonstrated above is unnecessarily tedious. In this case the solution may be carried out without conversion to molal or weight units by application of the concept of partial volumes. The total volume of any mixture may be obtained by adding together the volume which each of its components would occupy at the specified conditions of temperature and total pressure. Similarly, the removal of a component from a mixture will decrease the total volume by the volume which it alone would occupy at the existing conditions of temperature and total pressure. Care must be taken in the use of this method that all volumes which are added together are expressed *at the same conditions of temperature and pressure*. A process involving changes in temperature and pressure as well as composition is best considered as taking place in two steps: first, the change in composition at the initial conditions of temperature and pressure; and second, the change in

volume of the resultant mixture to correspond to the final conditions of temperature and pressure. Again the entire calculation must be based on a definite quantity of a component which passes through the process without change in quantity. This procedure is indicated in the following illustration:

Illustration 12. In the manufacture of hydrochloric acid a gas is obtained which contains 25% HCl and 75% air by volume. This gas is passed through an absorption system in which 98% of the HCl is removed. The gas enters the system at a temperature of 120° F and a pressure of 743 mm of Hg and leaves at a temperature of 80° F and a pressure of 738 mm of Hg.

a. Calculate the volume of gas leaving per 100 cu ft entering the absorption apparatus.

b. Calculate the percentage composition by volume of the gases leaving the absorption apparatus.

c. Calculate the weight of HCl removed per 100 cu ft of gas entering the absorption apparatus.

Solution:

Basis: 100 cu ft of entering gas (743 mm Hg, 120° F) containing 75 cu ft of air which will be unchanged in quantity.

Partial vol. of HCl.....	25 cu ft (743 mm Hg, 120° F)
Partial vol. of HCl absorbed.....	24.5 cu ft (743 mm Hg, 120° F)
Partial vol. of HCl remaining.....	0.50 cu ft (743 mm Hg, 120° F)

Vol. of gas remaining:

$$75 + 0.50 \dots\dots\dots 75.5 \text{ cu ft (743 mm, 120° F)}$$

Vol. of gas leaving:

$$75.5 \times \frac{743}{738} \times \frac{540}{580} \dots\dots\dots 70.8 \text{ cu ft (738 mm 80° F)}$$

Composition of gases leaving:

HCl, 0.5/75.5.....	0.66%
Air.....	99.34%

$$\text{Vol. at S.C. of HCl absorbed} = 24.5 \times \frac{743}{760} \times \frac{492}{580} \dots\dots\dots 20.3 \text{ cu ft}$$

$$\text{HCl absorbed} = 20.3/359 = 0.0565 \text{ lb-mol or} \dots\dots\dots 2.07 \text{ lb}$$

Partial Pressure Method. In certain types of work, especially where condensable vapors are involved, it is convenient to express the compositions of gaseous mixtures in terms of the partial pressures of the various components. Where data are presented in this form, problems of the type discussed above may be more conveniently solved by considering only the pressure changes resulting from the changes in composition. The addition or removal of a component of a mixture may be considered as producing only a change in the partial pressure of all of the other components. The *actual* volume occupied by each of these components will always be exactly the same as that of the entire mixture. The volume of

the mixture may then always be determined by application of the gas law to any components which pass through the process unchanged in quantity and whose partial pressures are known at both the initial and final conditions. The use of this method is shown in the following illustration.

Illustration 13. Calcium hypochlorite is produced by absorbing chlorine in milk of lime. A gas produced by the Deacon chlorine process enters the absorption apparatus at a pressure of 740 mm of Hg and a temperature of 75° F. The partial pressure of the chlorine is 59 mm of Hg, the remainder being inert gases. The gas leaves the absorption apparatus at a temperature of 80° F and a pressure of 743 mm of Hg with a partial pressure of chlorine of 0.5 mm of Hg.

- Calculate the volume of gases leaving the apparatus per 100 cu ft entering.
- Calculate the weight of chlorine absorbed, per 100 cu ft of gas entering.

Solution:

Basis: 100 cu ft of gas entering (740 mm Hg, 75° F).

Partial pressure of inert gases entering = 740 - 59.....	681 mm Hg
Partial pressure of inert gases leaving = 743 - 0.5.....	742.5 mm Hg
Actual volume of inert gas entering.....	100 cu ft
Actual volume of inert gases leaving = $100 \times \frac{681}{742.5} \times \frac{540}{535} = 92.5$ cu ft which	

also the total volume of gases leaving (743 mm Hg, 80° F).

The actual volumes of chlorine entering and leaving are also respectively 100 and 92.5 cu ft.

Volume at S.C. of chlorine entering = $100 \times \frac{59 \times 492}{760 \times 535}$	7.14 cu ft
Volume at S.C. of chlorine leaving = $92.5 \times \frac{0.5 \times 492}{760 \times 540}$	0.055 cu ft
Volume at S.C. of chlorine absorbed = 7.14 - 0.055.....	7.08 cu ft
Chlorine absorbed = $\frac{7.08}{359} = 0.0197$ lb-mol or	1.40 lb

GASES IN CHEMICAL REACTIONS

In a great many chemical and metallurgical reactions gases are present, either in the reacting materials or in the products or in both. Quantities of gases are ordinarily expressed in volume units because of the fact that the common methods of measurement give results directly on this basis. Similarly, gas analyses are ordinarily expressed on the volume basis, resulting directly from the data of the common analytical methods. The general types of reaction calculations must, therefore, include the complications introduced by the expression of gaseous quantities and compositions in volume units.

In Chapter II methods were demonstrated for the solution of reaction calculations through the use of molal units for the expression of quantities of reactants and products. Where this is the scheme of calculation, the introduction of volumetric data adds but few complications. By

the use of the normal molal volume constants combined with the proportions of the simple gas law it is easy to convert from molal to volume units, and the reverse. The methods of conversion have been explained in the preceding sections.

The same general methods of solution are followed as were described in Chapter II. All quantities of active materials, whether gaseous, solid, or liquid, are expressed in molal units and the calculation carried out on this basis. Results are thus obtained in molal units which may readily be converted to volumes at any desired conditions. The most convenient choice of a quantity of material to serve as the basis of calculation is determined by the manner of presentation of the data. In general, if the data regarding the basic material are in weight units, a unit weight is the best basis of calculation. If the data are in volume units, a unit molal quantity is ordinarily the most desirable

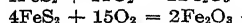
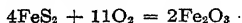
Illustration 14. For the production of sulphuric acid by the contact process, iron pyrites is burned in air to produce the dioxide and trioxide of sulphur. It is desired that air be supplied in 30% excess of that required for complete oxidation of the pyrites to Fe_2O_3 and SO_3 . It may be assumed in the operation of the burner that all the iron is completely oxidized and that 60% of the sulphur is burned to SO_2 and 40% to SO_3 .

a. Calculate the volume of air at 75° F and 14.7 lb per sq in. which must be supplied per 100 lb of pyrites burned.

b. Calculate the volume at 500° F and 14.6 lb per sq in. of the gases leaving the burner per 100 lb of pyrites burned.

c. Calculate the percentage composition by volume of the gaseous products leaving the burner.

† Basis of Calculation: 100 lb of FeS_2 or 0.834 lb-mol.



a. O_2 required = $15/4 \times 0.834$	3.12 lb-mols
O_2 supplied = 3.12×1.3	4.06 lb-mols
Air supplied = $\frac{4.06}{0.210}$	19.3 lb-mols
Volume of air, S.C. = 19.3×359	6930 cu ft
Volume of air, 75° F, 14.7 lb persq in. = $6930 \times \frac{535}{492}$...	7530 cu ft
b. Sulphur burned = 2×0.834	1.668 lb-atoms
SO_2 produced = 1.668×0.6	1.00 lb-mol
SO_3 produced.....	0.668 lb-mol

From the O_2 balance:

O_2 used in production of SO_2 = $(11/8) \times 1.00$	1.375 lb-mols
O_2 used in production of SO_3 = $(15/8) \times 0.668$	1.25 lb-mols
Total O_2 consumed.....	2.625 lb-mols

O ₂ remaining = 4.06 - 2.625	1.435 lb-mols
N ₂ present = 19.3 × 0.790	15.25 lb-mols
Total quantity of gases leaving burner = 1.00 + 0.668	
+ 1.435 + 15.25	18.35 lb-mols
Volume of gases, S.C. = 18.35 × 359	6590 cu ft
Volume of gases, 600° F, 14.6 lb per sq in. =	
$\frac{60 \times 14.7}{92 \times 14.6}$	12,920 cu ft

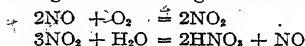
Composition of gases by volume:

SO ₂ = 1.00/18.35	5.45%
SO ₂ = 0.668/18.35	3.64%
O ₂ = 1.435/18.35	7.82%
N ₂ = 15.25/18.35	83.09%
	100.00%

Illustration 15. Nitric acid is produced in the Ostwald process by the oxidation of ammonia with air. In the first step of the process ammonia and air are mixed together and passed over a catalyst at a temperature of 700° C. The following reaction takes place:



The gases from this process are passed into towers where they are cooled and the oxidation completed according to the following theoretical reactions:



The NO liberated is in part reoxidized and forms more nitric acid in successive repetitions of the above reactions. The ammonia and air enter the process at a temperature of 20° C and a pressure of 755 mm Hg. The air is present in such proportion that the oxygen will be 20% in excess of that required for complete oxidation of the ammonia to nitric acid and water. The gases leave the catalyzer at a pressure of 743 mm of Hg and a temperature of 700° C.

a. Calculate the volume of air to be used per 100 cu ft of ammonia entering the process.

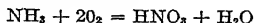
b. Calculate the percentage composition by volume of the gases entering the catalyzer.

c. Calculate the percentage composition by volume of the gases leaving the catalyzer, assuming that the degree of completion of the reaction is 85% and that no other decompositions take place.

d. Calculate the volume of gases leaving the catalyzer per 100 cu ft of ammonia entering the process.

e. Calculate the weight of nitric acid produced per 100 cu ft of ammonia entering the process, assuming that 90% of the nitric oxide entering the tower is oxidized to nitric acid.

Basis of Calculation: 1.0 lb-mol of NH₃.



a.	O ₂ required	2.0 lb-mols
	O ₂ supplied = 2.0 × 1.2	2.4 lb-mols
	Air supplied = $\frac{2.4}{0.210}$	11.42 lb-mols

Therefore:

Vol. of air = $11.42 \times$ (vol. of ammonia at same conditions)

or:

Vol. of NH_3 = $359 \times \frac{293 \times 760}{273 \times 755} = 388$ cu ft (20°C , 755 mm Hg)

Vol. of air = $11.42 \times 388 = 4440$ cu ft (20°C , 755 mm Hg)

Vol. of air per 100 cu ft of NH_3 = $\frac{4440 \times 100}{388} = 1142$ cu ft

b. Gases entering process = N_2 , O_2 , NH_3 .

N_2 present in air = 0.790×1142 9.02 lb-mols

Total quantity of gas entering catalyzer = $11.42 + 1$ 12.42 lb-mols

Composition by volume:

NH_3 = $1.0/12.42$ 8.0%

O_2 = $2.4/12.42$ 19.3%

N_2 = $9.02/12.42$ 72.7%

100.0%

c. Gases leaving catalyzer, N_2 , NH_3 , O_2 , NO , and H_2O .

NH_3 oxidized in catalyzer 0.85 lb-mol

NH_3 leaving catalyzer 0.15 lb-mol

O_2 consumed in catalyzer = $(5/4) \times 0.85$ 1.06 lb-mols

O_2 leaving catalyzer = $2.40 - 1.06$ 1.34 lb-mols

NO formed in catalyzer 0.85 lb-mol

H_2O formed in catalyzer = $(6/4) \times 0.85$ 1.275 lb-mols

Total quantity of gas leaving catalyzer = $9.02 + 0.15$
 $+ 1.34 + 0.85 + 1.275$ 12.64 lb-mols

Composition by volume:

NO = $0.85/12.64$ 6.7%

H_2O = $1.275/12.64$ 10.1%

NH_3 = $0.15/12.64$ 1.2%

O_2 = $1.34/12.64$ 10.6%

N_2 = $9.02/12.64$ 71.4%

Basis of Calculation: 100 cu ft of NH_3 entering the process.

d. Mols of NH_3 = $\frac{1.0 \times 100}{388}$ 0.258 lb-mol

Mols of gas leaving catalyzer = 0.258×12.64 3.26 lb-mols

Vol. at S.C. of gas leaving catalyzer = 3.26×359 1170 cu ft

Vol. of gas leaving catalyzer = $1170 \times \frac{760 \times 973}{743 \times 273}$ 4270 cu ft

(700°C , 743 mm Hg) per 100 cu ft of NH_3 entering.

e. NO produced in catalyzer = 0.258×0.85 0.219 lb-mol

NO oxidized in tower = 0.219×0.90 0.197 lb-mol

HNO_3 formed = 0.197 lb-mol or 0.197×63 12.4 lb

Range of Applicability of the Simple Gas Law. The simple gas law is applicable only at conditions of low pressure and high temperature

corresponding to large molal volumes at conditions resulting in small molal volumes. At conditions resulting in small molal volumes the simple kinetic theory breaks down and volumes calculated from the simple law tend to be too large. In extreme cases the calculated volume may be five times too great — an error of 400 per cent.

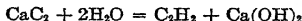
If an error of 1 per cent is permissible the simple law may be used for diatomic gases where gram-molal volumes are as low as 5 liters (80 cubic feet per pound-mol) and for gases of more complex molecular structure such as carbon dioxide, acetylene, ammonia, and the lighter hydrocarbon vapors, where gram-molal volumes exceed 20 liters (320 cubic feet per pound-mol).

The actual behavior of gases under high-pressure conditions is discussed in Chapter XI where rigorous methods of calculation are presented.

PROBLEMS

Pressures are absolute unless otherwise stated

1. It is desired to market oxygen in small cylinders having volumes of 0.5 cu. ft. and each containing 1.0 lb of oxygen. If the cylinders may be subjected to a maximum temperature of 120° F, calculate the pressure for which they must be designed, assuming the applicability of the simple gas law.
2. Calculate the number of cubic feet of hydrogen sulphide, measured at a temperature of 30° C and a pressure of 29.1 in. of Hg, which may be produced from 10 lb of iron sulphide (FeS).
3. An automobile tire is inflated to a gauge pressure of 35 lb per sq in. at a temperature of 0° F. Calculate the maximum temperature to which the tire may be heated without the gauge pressure exceeding 50 lb per sq in. (Assume that the volume of the tire does not change.)
4. Calculate the densities in pounds per cubic foot at standard conditions and the specific gravities of the following gases: (a) methane, (b) hydrogen, (c) acetylene, (d) bromine.
5. The gas acetylene is produced according to the following reaction by treating calcium carbide with water.



Calculate the number of hours of service which can be derived from 1.0 lb of carbide in an acetylene lamp burning 2 cu ft of gas per hour at a temperature of 75° F and a pressure of 743 mm of Hg.

6. A natural gas has the following composition by volume:

CH ₄	94.1%
N ₂	3.0%
H ₂	1.9%
O ₂	1.0%
	<hr/>
	100.0%

This gas is piped from the well at a temperature of 20° C and a pressure of 30 lb per sq in. It may be assumed that the simple gas law is applicable.

- Calculate the partial pressure of the oxygen.
- Calculate the partial volume of nitrogen per 100 cu ft of gas.
- Calculate the density of the mixture in pounds per cubic foot at the existing conditions.

7. A gas mixture contains 0.274 lb-mol of HCl, 0.337 lb-mol of nitrogen, and 0.081 lb-mol of oxygen. Calculate the volume occupied by this mixture and its density in pounds per cubic foot at a pressure of 40 lb per sq in. and a temperature of 30° C

8. A chimney gas has the following composition by volume:

CO ₂	10.5%
CO	1.1%
O ₂	7.7%
N ₂	80.7%

Using the simple gas law, calculate:

- Its composition by weight.
- The volume occupied by 1.0 lb of the gas at 67° F and 29.1 in. of Hg pressure
- The density of the gas in pounds per cubic foot at the conditions of part b
- The specific gravity of the mixture.

9. By electrolyzing a mixed brine a mixture of gases is obtained at the cathode having the following composition by weight:

Cl ₂	67%
Br ₂	28%
O ₂	5%

Using the simple gas law, calculate:

- The composition of the gas by volume.
- The density of the mixture in grams per liter at 25° C and 740 mm of Hg pressure.
- The specific gravity of the mixture.

10. A mixture of ammonia and air at a pressure of 745 mm of Hg and a temperature of 40° C contains 4.9% NH₃ by volume. The gas is passed at a rate of 100 cu ft per min through an absorption tower in which only ammonia is removed. The gases leave the tower at a pressure of 740 mm of Hg, a temperature of 20° C, and contain 0.13% NH₃ by volume. Using the simple gas law, calculate:

- The rate of flow of gas leaving the tower in cubic feet per minute.
- The weight of ammonia absorbed in the tower per minute.

11. A volume of moist air of 1000 cu ft at a total pressure of 740 mm of Hg and a temperature of 30° C contains water vapor in such proportions that its partial pressure is 22.0 mm of Hg. Without changing the total pressure, the temperature is reduced to 15° C and some of the water vapor removed by condensation. After cooling it is found that the partial pressure of the water vapor is 12.7 mm of Hg. Using the partial pressure method, calculate:

- The volume of the gas after cooling.
- The weight of water removed.

12. Air is passed into a drier for the drying of textiles at a rate of 1000 cu ft per min. The air enters the drier at a temperature of 160° F and contains water vapor

exerting a partial pressure of 8.1 mm of Hg. The temperature of the air leaving is 80° F, and the partial pressure of the water is 18 mm of Hg. The total pressure of the wet air may be taken as constant at the barometric value of 745 mm of Hg.

- a. Calculate the volume of gas leaving the drier per minute.
- b. Calculate the weight of water removed per minute from the material in the drier.

13. A producer gas has the following composition by volume:

CO	23.0%
CO ₂	4.4%
O ₂	2.6%
N ₂	70.0%

- a. Calculate the cubic feet of gas, at 70° F and 750 mm of Hg pressure, per pound of carbon present.
- b. Calculate the volume of air at the conditions of part a, required for the combustion of 100 cu ft of the gas at the same conditions if it is desired that the total oxygen present before combustion shall be 20% in excess of that theoretically required.
- c. Calculate the percentage composition by volume of the gases leaving the burner of part b, assuming complete combustion.
- d. Calculate the volume of the gases leaving the combustion of parts b and c at a temperature of 600° F and a pressure of 750 mm of Hg per 100 cu ft.

SO ₂	1.1%
SO ₃	8.2%
O ₂	10.0%
N ₂	80.7%

- a. Calculate the volume of the gas at 350° F and 29.2 in. of Hg formed per pound of sulphur burned.
- b. Calculate the percentage excess oxygen supplied for the combustion above that required for complete oxidation to SO₃.
- c. From the above gas analysis calculate the percentage composition by volume of the air used in the combustion.
- d. Calculate the volume of air at 70° F and 29.2 in. of Hg supplied for the combustion per pound of sulphur burned.

15. A furnace is to be designed to burn coke at the rate of 200 lb per hour. The coke has the following composition:

Carbon	89.1%
Ash	10.9%

The grate efficiency of the furnace is such that 90% of the carbon present in the coke charged is burned. Air is supplied in 30% excess of that required for the complete combustion of all the carbon charged. It may be assumed that 97% of the carbon burned is oxidized to the dioxide, the remainder forming monoxide.

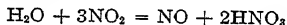
- a. Calculate the composition, by volume, of the flue gases leaving the furnace.
- b. If the flue gases leave the furnace at a temperature of 550° F and a pressure of 743 mm Hg, calculate the rate of flow of gases, in cubic feet per minute, for which the stack must be designed.

16. Coke containing 87.2% carbon and 12.8% ash is burned on a grate. It is found that 6% of the carbon in the coke charged is lost with the refuse. The composition by volume of the stack gases from the furnace is as follows:

CO ₂	12.0%
CO	0.2%
O ₂	8.8%
N ₂	79.0%

- Calculate the volume of gases, at 540° F and 29.3 in. of Hg pressure, formed per pound of coke charged.
- Calculate the per cent of excess air supplied above that required for complete oxidation of the carbon charged.
- Calculate the degree of completion of the oxidation, to the dioxide, of the carbon burned.
- Calculate the volume of air, at 70° F and 29.3 in. Hg, supplied per pound of coke charged.

17. In the fixation of nitrogen by the arc process, air is passed through a magnetically flattened electric arc. Some of the nitrogen is oxidized to NO which on cooling oxidizes to NO₂. Of the NO₂ formed, 66% will be associated to N₂O₄ at 26° C. The gases are then passed into water-washed absorption towers where nitric acid is formed by the following reaction:



The NO liberated in this reaction will be reoxidized in part and form more nitric acid

In the operation of such a plant it is found possible to produce gases from the arc furnace in which the nitric oxide is 2% by volume, while hot. The gases are cooled to 26° C at a pressure of 750 mm of Hg before entering the absorption apparatus.

- Calculate the complete analysis by volume of the hot gases leaving the furnace assuming that the air entering the furnace was of average atmospheric composition.
- Calculate the partial pressures of the NO₂ and N₂O₄ in the gas entering the absorption apparatus.
- Calculate the weight of HNO₃ formed per 1000 cu ft of gas entering the absorption system if the conversion to nitric acid of the combined nitrogen in the furnace gases is 85% complete.

CHAPTER IV

VAPORIZATION AND CONDENSATION

Liquefaction and the Liquid State. Molecules in the gaseous state of aggregation exhibit two opposing tendencies. The translational kinetic energy possessed by each molecule represents a continual, random motion which tends to separate the molecules from one another and to cause them to be uniformly distributed throughout the entire available space. On the other hand, the attractive forces between the molecules tends to draw them together into a concentrated mass, not necessarily occupying the entire space which is available. The first tendency, that of dispersion, is dependent entirely on the temperature. An increase in the temperature will increase the translational kinetic energy of each molecule and will therefore give it an increased ability to overcome the forces tending to draw it toward other molecules.

The second tendency, that of aggregation, is determined by the magnitudes and nature of the attractive forces between the molecules and by their proximity to one another. These intermolecular attractive forces are believed to be of such a nature that they increase to definite maxima as the distances between molecules are diminished. This behavior is shown in Fig. 2, in which are plotted attractive forces as ordinates and distances of separation between two molecules as abscissas. The greatest attractive force between the two molecules exists when they are separated by a relatively small distance S_2 . If the distance of separation is diminished below S_2 , the attractive force rapidly decreases and will reach high negative values corresponding to repulsion. At a distance of separation S_1 the attractive force becomes zero, corresponding to a position of equilibrium. If unaffected by other forces, molecules will group themselves together, separated from one another by distances equal to S_1 . Any attempt made to crowd them closer together will meet with repulsive forces. In order to separate them by a distance greater than S_2 it would be necessary to overcome the maximum attractive force by heating or expansion.

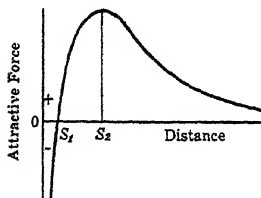


FIG. 2. Attractive Force
Between Molecules.

When a gas is isothermally compressed and the distances of separation between the molecules are decreased, the attractive forces increase toward their maximum value. If these attractive forces become large enough that the potential energy of the attraction of one molecule for another is greater than its kinetic energy of translation, the molecules will be held together to form a dense aggregation which is termed a *liquid*. The characteristic which differentiates a liquid from a gas is the fact that the liquid possesses a definite volume and does not necessarily occupy the entire available space. The individual molecules of the liquid are in motion, owing to their inherent kinetic energies, but this motion takes the form of vibrations, alternately increasing and decreasing the distances of separation, as though energized, vibrating marbles were attached to each other by short rods of rubber.

Critical Temperature and Pressure. Whether or not a substance can exist in the liquid state is dependent on the temperature. If the temperature is sufficiently high that the kinetic energies of translation of the molecules exceed the *maximum* potential energy of attraction between them, the liquid state of aggregation is impossible. The temperature at which the molecular kinetic energy of translation equals the maximum potential energy of attraction is termed the *critical temperature*, t_c . Above the critical temperature the liquid state is impossible and compression results only in a highly compressed gas, retaining all the properties of the gaseous state. Below the critical temperature a gas may be liquefied if sufficiently compressed.

The pressure required to liquefy a gas at its critical temperature is termed the *critical pressure*, p_c . The critical pressure and temperature fix the *critical state* at which there is no distinction between the gaseous and liquid states. The volume at the critical state is termed the *critical volume*, v_c . The density at the critical state is the *critical density*, d_c . In Table XIX, page 383, are values of the critical data for the more common gases.

VAPOR PRESSURE

As pointed out above, the liquid state results when conditions are such that the potential energies of attraction between molecules exceed their kinetic energies of translation. These conditions are brought about when the temperature of a substance is lowered, decreasing the kinetic energies of translation, or when the molecules are crowded close together, increasing the energies of attraction. On the basis of this theory the surface of a liquid may be pictured as a layer of molecules, each of which is bound to the molecules below it by the attractive forces among them. One of the surface molecules may be removed only by

overcoming the attractive forces holding it to the others. This is possible if the molecule is given sufficient translational kinetic energy to overcome the maximum potential energy of attraction and to enable it to move past the point of maximum attraction. Once it has passed this distance of maximum attraction, the molecule is free to move away from the surface under the effect of its translational energy and it becomes a gas molecule.

In the simple kinetic-theory mechanisms which have been discussed, it has been assumed that all molecules of a substance at a given temperature are endowed with the same kinetic energies and move at the same speeds. Actually it has been demonstrated that this is not the case and that molecular speeds and energies vary over wide ranges above and below the average values. In every liquid and gas there are always highly energized molecules moving at speeds much higher than the average. When such a molecule comes to the surface of a liquid, with its velocity directed away from the main body, it may have sufficient energy to break away completely from the forces tending to hold it to the surface. This phenomenon of the breaking away of highly energized molecules takes place from every exposed liquid surface. As a result, the matter of the liquid continually tends to assume the gaseous or vapor state. This phenomenon is termed *vaporization* or *evaporation*.

When a liquid evaporates into a space of limited dimensions the space will become filled with the vapor which is formed. As vaporization proceeds, the number of molecules in the vapor state will increase and cause an increase in the pressure exerted by the vapor. It will be recalled that the pressure exerted by a gas or vapor is due to the impacts of its component molecules against the confining surfaces. Since the original liquid surface forms one of the walls confining the vapor, there will be a continual series of impacts against it by the molecules in the vapor state. The number of such impacts will be dependent on or will determine the pressure exerted by the vapor. However, when one of these gaseous molecules strikes the liquid surface it comes under the influence of the attractive forces of the densely aggregated liquid molecules and will be held there, forming a part of the liquid once more. This phenomenon, the reverse of vaporization, is known as *condensation*. The rate of condensation is determined by the number of molecules striking the liquid surface per unit time, which in turn is determined by the pressure or density of the vapor. It follows that when a liquid evaporates into a limited space, two opposing processes are in operation. The process of vaporization tends to change the liquid to the gaseous state. The process of condensation tends to change the gas which is formed by vaporization back into the liquid state. The rate of conden-

sation is increased as vaporization proceeds and the pressure of the vapor increases. If sufficient liquid is present, the pressure of the vapor must ultimately reach such a value that the rate of condensation will equal the rate of vaporization. When this condition is reached, a dynamic equilibrium is established and the pressure of the vapor will remain unchanged, since the formation of new vapor is compensated by condensation. If the pressure of the vapor is changed in either direction from this equilibrium value it will adjust itself and return to the equilibrium conditions owing to the increase or decrease in the rate of condensation which results from the pressure change. The pressure exerted by the vapor at such equilibrium conditions is termed the *vapor pressure* of the liquid. All materials exhibit definite vapor pressures of greater or less degree at all temperatures.

The magnitude of the equilibrium vapor pressure is in no way dependent on the amounts of liquid and vapor as long as any free liquid surface is present. This results from both the rate of loss and the rate of gain of molecules by the liquid being directly proportional to the area exposed to the vapor. At the equilibrium conditions when both rates are the same, a change in the area of the surface exposed will not affect the conditions in the vapor phase. The nature of the liquid is the most important factor determining the magnitude of the equilibrium vapor pressure. Since all molecules are endowed with the same kinetic energies of translation at any specified temperature, the vapor pressure must be entirely dependent on the magnitudes of the attractive forces between the molecules. The maximum potential energies of attraction which must be overcome in vaporization are determined by these forces. Thus, if a substance has high intermolecular attractive forces the rate of loss of molecules from its surface should be small and the corresponding equilibrium vapor pressure low. The magnitudes of the attractive forces are dependent on both the size and nature of the molecules, usually increasing with increased size and complexity. In general, among liquids of similar chemical natures, the vapor pressure at any specified temperature decreases with increasing molecular weight.

EFFECT OF TEMPERATURE ON VAPOR PRESSURE

The forces causing the vaporization of a liquid are entirely derived from the kinetic energy of translation of its molecules. It follows that an increase in kinetic energy of molecular translation should increase the rate of vaporization and therefore the vapor pressure. In Chapter III it was pointed out that the kinetic energy of translation is directly proportional to the absolute temperature. On the basis of this theory, an

increase in temperature should cause an increased rate of vaporization and a higher equilibrium vapor pressure. This is found to be universally the case where vapor pressures have been experimentally investigated. It must be remembered that it is the temperature of the *liquid surface* which is effective in determining the rate of vaporization and the vapor pressure.

The actual relationship between vapor pressure and temperature is of a very complicated nature. An exact thermodynamic equation giving this relationship is

$$\left(\frac{\delta p}{\delta T}\right)_s = \frac{L_v}{T(V_g - V_l)} \quad (1)$$

where

p = vapor pressure

T = absolute temperature

R = gas constant

L_v = latent heat of vaporization at temperature T

V_g = volume of gas

V_l = volume of liquid

Neglecting the volume of liquid and assuming the applicability of the ideal gas law the above relation reduces to the Clausius-Clapeyron equation:

$$\frac{dp}{p} = \frac{L_v dT}{T^2} \quad (2)$$

The latent heat of vaporization is the heat required to change one gram-mol of a substance from the liquid to the vapor state at the same temperature. The nature of this property will be discussed in Chapter V. (Values of the latent heat of vaporization for many materials may be found in Table VIII, page 138.) The Clausius-Clapeyron equation in the form written above is accurate only when the vapor pressure is relatively low so that it may be assumed that the vapor obeys the simple gas law and that the volume in the liquid state is negligible as compared to that of the vapor state.

Where the temperature does not vary over wide limits it may be assumed that the latent heat of vaporization, L_v , is constant and Equation (2) integrated, between the limits p_0 , T_0 and p , T . Then,

$$\begin{aligned} \ln \frac{p}{p_0} &= \frac{L_v}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \\ \text{or} \quad &= \frac{L_v}{2.303R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \end{aligned} \quad (3)$$

Equation (3) permits calculation of the vapor pressure of a substance at a temperature T if the vapor pressure p_0 at another temperature T_0

is known, together with the latent heat of vaporization L_v . The results are accurate only over limited ranges of temperature in which it may be assumed that the latent heat of vaporization is constant and at such conditions that the simple gas law is obeyed.

Illustration 1. The vapor pressure of ethyl ether is given in the International Critical Tables as 185 mm of Hg at 0° C. The latent heat of vaporization is 92.5 calories per gram at 0° C. Calculate the vapor pressure at 20° C and at 35° C.

Molecular weight	74.
L_v	6850 calories per gram-mol.
R	1.99 calories per gram-mol per °K.
T_0	273° K.
p_0	185 mm Hg.

when

$$T = 293^\circ \text{ K (20}^\circ \text{ C)}$$

$$\frac{p}{185} = \frac{6850}{2.30 \times 1.99} \left[\frac{1}{273} - \frac{1}{293} \right] = 1495 (0.003663 - 0.003413) = 0.374$$

$$\frac{p}{185} = 2.36 \qquad p = 437 \text{ at } 20^\circ \text{ C}$$

when

$$T = 308^\circ \text{ K (35}^\circ \text{ C)}$$

$$\log \frac{p}{185} = 1495 (0.003663 - 0.003247) = 0.621$$

$$\frac{p}{185} = 4.18 \qquad p = 773 \text{ mm Hg at } 35^\circ \text{ C}$$

The values for the vapor pressure of ether which have been experimentally observed are 442 mm of Hg at 20° C and 775.5 mm of Hg at 35° C. In this particular case the Clausius-Clapeyron equation yields results which are satisfactory for many purposes. However, the equation is only an approximation which may lead to considerable error in some cases. It should be used only in the absence of experimental data.

The more complete tables of physical data contain experimentally determined values of the vapor pressures of many substances at various temperatures. From these data empirical curves may be plotted which accurately express vapor pressures as functions of temperature. From such a curve, vapor pressure may be determined at any desired temperature in the range investigated. However, a curve relating values of the vapor pressure and temperatures when plotted on ordinary uniform scales of coordinates is not convenient for use. Values of vapor pressures vary over such wide ranges that a single chart cannot be used to represent the relationship over a considerable temperature range without sacrifice of accuracy at the lower temperatures. Furthermore, the rapidly changing slope of such a curve makes extrapolation very uncertain.

These disadvantages of the vapor-pressure curve when plotted on uni-

form scales of coördinates may be overcome by special methods of plotting. A method which has been extensively used is to plot values of the logarithms of the vapor pressures ($\log p$) against the reciprocals of the absolute temperatures ($1/T$). Such curves are approximately straight lines over considerable ranges of temperature. Another method is to plot the logarithms of the pressures against the logarithms of the absolute temperatures. Both these methods yield curves which show but little curvature and which may be read accurately over wide ranges of temperature.

The Cox Chart. A method of plotting which was proposed by Cox¹ has the advantage of producing approximately straight lines which, for a series of similar compounds, converge at a single point. In this method an ordinary logarithmic scale is used for plotting vapor pressures as ordinates. The temperatures are plotted as abscissas, on a non-uniform scale, so selected that the curve representing the vapor pressure of an arbitrarily chosen reference substance will be a straight line. Water serves as a convenient reference substance for which extensive data are available. The procedure for constructing such a chart is as follows: A logarithmic scale covering the desired range of vapor pressures is laid out along one edge of an unruled sheet of paper. Horizontal coördinate lines are ruled across the sheet from the division points on this scale. A straight line is drawn passing to the left of the center of the sheet and sloping upward to the right at an angle of about 45 degrees. This is adopted as the vapor pressure curve of water. The scale of abscissas is then laid out from the experimental data for the vapor pressure of water. For example, the point representing 100° C on the scale of abscissas will correspond to the point at which the reference curve crosses the ordinate corresponding to 760 millimeters of mercury. In this manner the entire scale of abscissas may be laid out and the vertical coördinate lines ruled on the sheet. With both coördinate scales established, curves representing the vapor pressure data of any other substances may be plotted on the same sheet.

The Cox method of plotting has been studied by Calingaert and Davis,² who found that the data for widely varying types of materials yield lines with practically no curvature when plotted on such a chart. Furthermore, it was found that the curves of groups of closely related compounds converge at single points which are characteristic of the groups. For example, single points of convergence were found for each of the following groups: the paraffin hydrocarbons, the benzene monohalides, the alcohols, the silicon hydride series, and the metals.

¹ E. R. Cox, *Ind. Eng. Chem.* **15**, 592 (1923).

² *Ind. Eng. Chem.* **17**, 1287 (1925).

Calingaert and Davis also found that the method of Cox is equivalent to assuming that the vapor pressure of any substance is represented by the following equation:

where

$$\begin{aligned}p &= \text{vapor pressure} \\t &= \text{temperature, } ^\circ\text{C} \\A, C &= \text{empirical constants}\end{aligned}$$

Thus, by plotting $\log p$ against $1/(t + 230)$ a straight line should be obtained. Two experimental values are sufficient to establish such a line.

In Fig. 3 data from the International Critical Tables for the vapor pressures of various substances are plotted by the method of Cox. In order to establish the scale of temperatures above 374°C , the critical temperature of water, the vapor-pressure data of mercury were used as a standard. On such a chart the entire vapor pressure curve of a substance may be predicted if two experimental points are available. For a member of a group of materials having convergent curves only one experimental point and the point of convergence of the group are necessary to establish a complete curve.

Illustration 2. The vapor pressure of chloroform is 61.0 mm of Hg at 0°C and 526 mm of Hg at 50°C . Estimate, from Fig. 3, the vapor pressure at 100°C .

Solution: The two experimental values of the vapor pressures at 0°C and 50°C are represented by points on Fig. 3. A straight line is projected through these two points to the ordinate representing 100°C . The abscissa at this point is approximately 2450 mm of Hg, the estimated vapor pressure at 100°C . The experimentally observed value is 2430 mm of Hg.

Illustration 3. The vapor pressure of normal butyl alcohol at 40°C is 18.6 mm of Hg. Estimate the temperature at which the vapor pressure is 760 mm of Hg, the normal boiling-point.

Solution: The experimental value of the vapor pressure at 40°C is represented by a point on Fig. 3. A straight line is drawn from this point to the point of convergence of the alcohol group. This point of convergence is located by extending the curves for methyl and propyl alcohols. The abscissa of the point at which this line crosses the 760-mm ordinate is about 117°C . The experimentally observed boiling-point of normal butyl alcohol is 117.7°C .

In the application of the Cox chart, or modifications of it such as Fig. 3, to the extrapolation of vapor-pressure data for hydrocarbons, it has been found that the correlation is not good for extremely high- or low-boiling compounds. For more reliable results on hydrocarbons and petroleum fractions Coats and Brown¹ developed a chart in which temperature

¹ Coats and Brown, "A Vapor Pressure Chart for Hydrocarbons," Dept. Engr. Research, University of Michigan, Circular Series No. 2 (December, 1928).

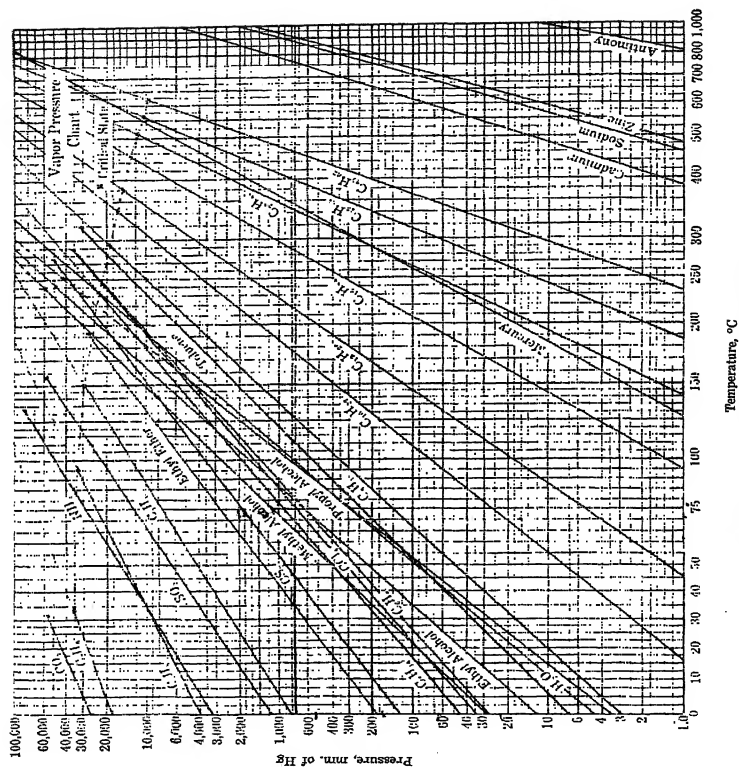


Fig. 3. Cox Vapor-Pressure Chart.

is plotted against normal boiling-point for a series of constant vapor pressures. It is believed that this method of plotting is the most satisfactory available. However, the resultant chart is somewhat cumbersome and difficult to read.

The chart shown in Fig. 4 was derived from the Brown-Coats chart by making both the abscissa and ordinate scales empirical in order to

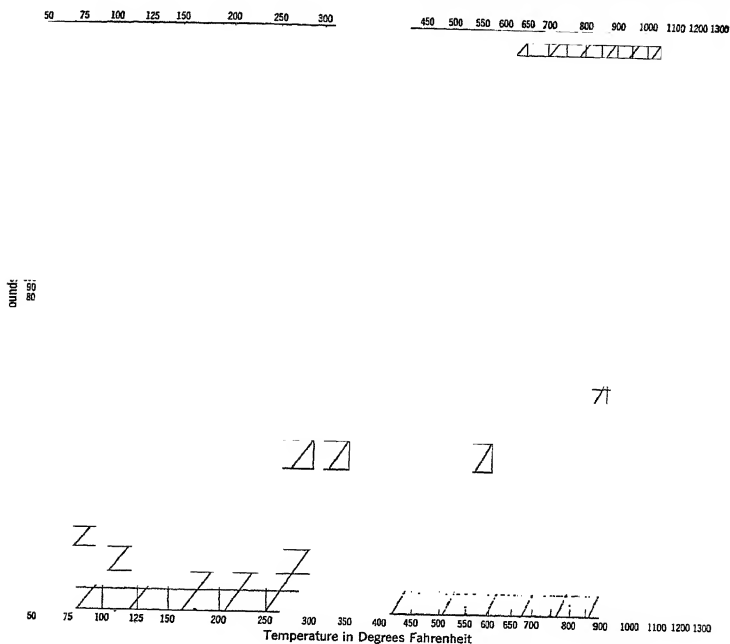


FIG. 4. Vapor Pressure of Hydrocarbons.

obtain the best agreement possible in a rectangular plot of this type. The sloping lines on this chart represent hydrocarbons of uniformly spaced normal boiling-points rather than particular compounds of any specific series. However, it is used in the same manner as Fig. 3, permitting the estimation of the complete vapor-pressure curve of a hydrocarbon from a single point. It is believed that the results of Fig. 4 are more reliable than those of the hydrocarbon lines of Fig. 3, particularly for the higher-boiling compounds.

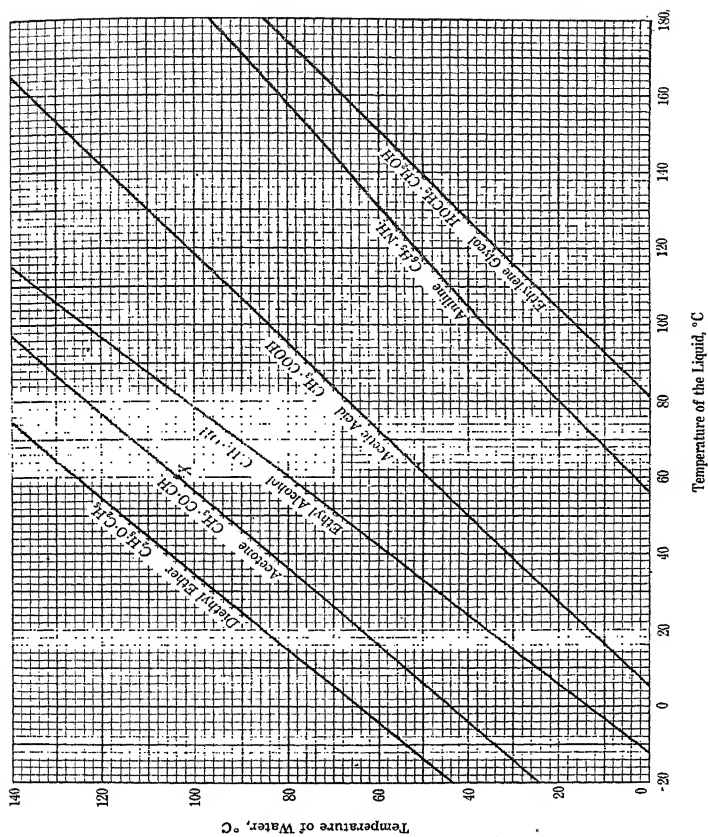
Dühring Lines. Another valuable method for plotting vapor-pressure data was first proposed by Dühring. Temperatures of the material in question are plotted as abscissas on a uniform scale. As ordinates are plotted the temperatures at which a selected reference substance has the same vapor pressure as does the material in question. Dühring lines of several substances are plotted in Fig. 5, using water as the reference substance. Each one of these lines relates the temperature of the designated substance to the temperature at which water exerts the same vapor pressure. In order to plot or use such a chart, complete vapor-pressure data must be available for the reference substance. The vapor-pressure curve of water is plotted in Fig. 6. From this curve the Dühring line of a substance may be readily established if its vapor pressures at several temperatures are known. For example, acetone at a temperature of 60°C exerts a vapor pressure of 861 millimeters of mercury. From Fig. 6 it is seen that water exerts this same vapor pressure at a temperature of about 104°C . These data locate point *x* on Fig. 5.

It will be noted that the lines of Fig. 5 are approximately straight. For this reason only two experimental values are necessary in order to establish the complete vapor-pressure curve of a substance. The use of the curves is not difficult. For example, if it is desired to determine the vapor pressure of acetone at 40°C , it is seen from Fig. 5 that this pressure will be the same as that of water at 84°C . The pressure is read from Fig. 6 as 430 millimeters of mercury. Similarly, the temperature at which acetone exerts a vapor pressure of 100 millimeters of mercury may be determined. From Fig. 6 it is seen that water exerts this pressure at a temperature of 52°C . From Fig. 5, acetone will exert the same pressure at 9°C .

The Dühring line permits the extension of limited vapor-pressure data over wide ranges and thus serves the same general purpose as the Cox chart. The Dühring line possesses the advantage of being much simpler to construct than a Cox chart but it is not as convenient for use. Furthermore, the Dühring lines of homologous series do not exhibit the convergency shown on the Cox chart.

Superheat and Quality. A vapor which exists above its critical temperature is termed a gas. The distinction between a vapor and a gas is thus quite arbitrary, and the two terms are loosely interchanged. For example, carbon dioxide at room temperature is below its critical temperature and, strictly speaking, is a vapor. However, such a material is commonly referred to as a gas.

A vapor which exists under such conditions that its partial pressure is equal to its equilibrium vapor pressure is termed a *saturated vapor*,



Temperature of the Liquid, °C

Fig. 5. Dühring Lines.

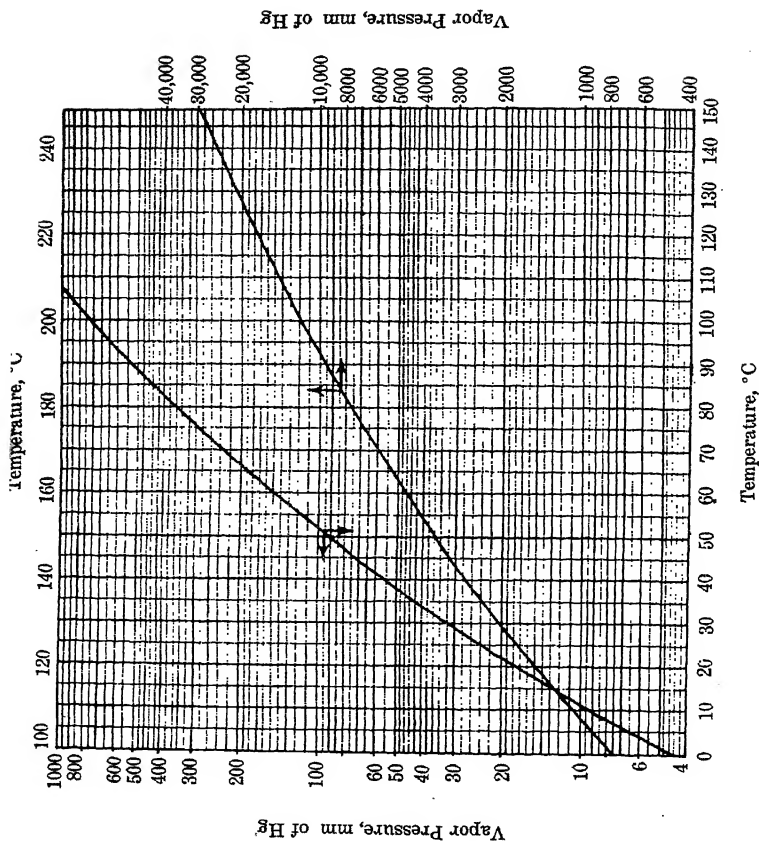


FIG. 6. Vapor Pressure of Water.

whether it exists alone or in the presence of other gases. The temperature at which a vapor is saturated is termed the *dew-point* or *saturation temperature*. A vapor whose partial pressure is less than its equilibrium vapor pressure is termed a *superheated vapor*. The difference between its existing temperature and its saturation temperature is called its *degrees of superheat*.

If a saturated vapor is cooled or compressed, condensation will result, and what is termed a *wet vapor* is formed. If the vapor is in turbulent motion considerable portions of the condensed liquid will remain in mechanical suspension as small drops in the vapor and be carried with it. The *quality* of a wet vapor is the percentage which the weight of a vapor forms of the total weight of vapor and entrained liquid associated with it. Thus, wet steam of 95 per cent quality is a mixture of saturated water vapor and entrained drops of liquid water in which the weight of the vapor constitutes 95 per cent of the total weight.

Estimation of Critical Temperatures from Boiling-Points. The critical temperature of a substance is of considerable value in predicting its behavior in certain types of industrial processes and in establishing relationships among other of its physical properties. However, the experimental determination of critical temperatures is difficult, and these data are not available for many substances. It is frequently desirable to attempt to predict the critical temperature of a substance from other, more easily determined properties. Guldberg proposed a rule that the ratio of the boiling-point, under a pressure of one atmosphere, to the critical temperature is a constant when both are expressed on an absolute scale of temperature. This rule is only a very rough approximation which cannot be used where reliable results are required.

In a method proposed by Watson¹ the critical temperature of a *non-polar* compound is predicted from its boiling-point, molecular weight, and liquid density. A non-polar compound is one having its atoms symmetrically arranged in the molecule so that there are no unbalanced electrical charges which tend to rotate the molecule when in an electrostatic field. Non-polar compounds are, in general, chemically inactive and do not ionize or conduct electricity well. For example, the hydrocarbons of practically all series are relatively non-polar, whereas water, alcohol, ammonia, and the like are highly polar. In general, compounds having symmetrical molecular arrangements such as methane (CH_4) or carbon tetrachloride (CCl_4) may be expected to have non-polar characteristics. Compounds of low molecular weight which do not have symmetrical molecular arrangements such as methyl chloride (CH_3Cl) or ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) or acetic acid (CH_3COOH) may be expected

¹ Ind. Eng. Chem. **23**, 360 (1931).

to be polar. Polar compounds do not follow many of the generalizations which apply to the non-polar group.

The following empirical equation was proposed:

$$\left(\frac{T_c}{T_b} \right)^{0.18} = \frac{M}{d} \quad (5)$$

where:

T_c = critical temperature ($^{\circ}\text{K}$).

T_b = the temperature ($^{\circ}\text{K}$) at which the substance is in equilibrium with its saturated vapor in a concentration of one gram-mol in 22.4 liters.

M = molecular weight.

d = density of the liquid in grams per cubic centimeter at its normal boiling-point.

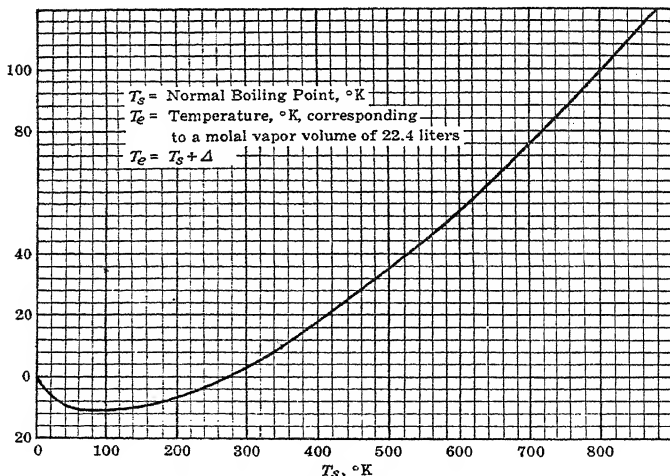


FIG. 7. Temperatures of Constant Vapor Concentration.

The temperature T_e is a function of the normal boiling-point of the substance. In Fig. 7 a curve is plotted relating $(T_e - T_b)$ to T_b , where T_b is the normal boiling-point in degrees Kelvin. From this curve T_e can be determined for any substance of known boiling-point. The density at the boiling-point may be determined or estimated from liquid density measurements at other temperatures. It was shown that Equation (5) permits prediction of critical temperatures of non-polar sub-

stances ranging from oxygen (boiling-point 90.1° K) to octane (boiling-point 398° K) with errors rarely exceeding 2.0 per cent. Good results were also obtained for slightly polar substances such as carbon disulphide and chlorbenzene, but the method breaks down when applied to highly polar substances such as water, ammonia, or the lower alcohols.

Illustration 4. Carbon tetrachloride has a normal boiling-point of 77° C and a liquid density at its boiling-point of 1.48 g per cc. Calculate the critical temperature.

$$T_s = 77 + 273 = 350^{\circ} \text{ K}$$

From Equation (5),

$$T_c = 550^{\circ} \text{ K or } 277^{\circ} \text{ C}$$

The experimentally observed value is 283° C.

EFFECT OF TOTAL PRESSURE ON VAPOR PRESSURE

The case considered in the preceding sections is that in which a liquid is in contact with a free space, containing no gases other than the vapor of the liquid. In this case the pressure of the vapor, and therefore the total pressure on the surface of the liquid, cannot exceed the equilibrium vapor pressure at the existing temperature. However, when a liquid is in contact with a limited space which is filled with some other gaseous material, the total pressure on the surface of the liquid may be indefinitely greater than the equilibrium vapor pressure. In this case the total pressure at equilibrium is the sum of the equilibrium vapor pressure and the partial pressure of this other gas. It is determined by the amount of gas present in the available volume and may be any finite value.

The presence of other gases above a liquid surface is known to have an effect on the equilibrium vapor pressure of the liquid which is a function of the total pressure of the gas on the liquid surface. In general, it is found that the equilibrium vapor pressure is increased by an increase in total pressure. The effect is small at low pressures and in general may be neglected where the total pressure on the liquid surface is less than 10 atmospheres. Under such conditions the presence of other gases in contact with the liquid will have no appreciable effect unless chemical reaction takes place between the gases and the liquid.

Larson and Black¹ have made an experimental study of the equilibrium concentrations of ammonia in compressed mixtures of hydrogen and nitrogen over liquid ammonia. The values of the apparent vapor pressure of liquid ammonia under high total pressures were found to be very much higher than the normal vapor pressures exerted when in contact with only pure vapor. At a total pressure of 50 atmospheres the apparent vapor pressure at 0° C was found to be 17 per cent greater than the normal value. At a total pressure of 1000 atmospheres the apparent vapor pressures were five times as great as the normal values.

The above authors offered three possible explanations for these results:

1. The vapor pressure of a pure liquid is increased by the application of external pressure.

¹J. Am. Chem. Soc. **47**, 1015-20 (1925).

2. The highly compressed gas may exert a specific solvent action in dissolving some of the liquid.

3. The presence of even a chemically indifferent gas may change the molecular aggregation in the vapor state through promotion of association.

It is apparent from these results that for systems under pressures greater than about 10 atmospheres the effects of external pressure on apparent equilibrium vapor pressures cannot be neglected where reasonable accuracy is required.

An approximate equation expressing the effect of total pressure upon vapor pressure is as follows:

$$\left(\frac{\delta p}{\delta P}\right)_T = \frac{v_l}{v_g} \quad (6)$$

where

p = vapor pressure of liquid

P = total pressure on liquid

v_l = molal volume of liquid

v_g = molal volume of vapor

EFFECT OF CURVATURE OF THE LIQUID SURFACE ON VAPOR PRESSURE

At ordinary values of total pressure, the equilibrium vapor pressure of a substance which is bounded by a plane surface is a function only of the nature of the substance and its temperature. However, it may be demonstrated from the capillary-rise phenomena of liquids that vapor pressure must also be a function of the radius of curvature of the liquid surface. This effect is negligible except in cases of very small radii of curvature such as are possessed by particles of submicroscopic dimensions. If the liquid surface is convex the vapor pressure is greater than for a plane surface. The vapor pressures of small droplets of a liquid may be many times greater than the normal value above a plane surface. If concave liquid surfaces are produced the vapor pressure is correspondingly diminished below the value of a plane surface.

The high vapor pressure possessed by very small liquid drops explains the fact that, if proper precautions are observed, a vapor may be *super-cooled* below its dew-point without condensing. A supercooled vapor is in an unstable condition, and once condensation is started it will proceed rapidly until equilibrium conditions are reached. However, if all traces of liquid are excluded from the vapor, condensation will take place only when several molecules collide and form a cluster. The vapor pressure of such a small cluster of molecules may be much greater than the existing pressure of the vapor, and the cluster will immediately break up through vaporization. Thus no permanent condensation can take place, even though the pressure of the vapor is much greater than the normal vapor pressure of the liquid above a plane surface. Supercooling is rarely encountered in industrial practice. Dust particles and many types of solid surfaces will absorb molecules of vapor and form starting-points or nuclei for condensations, which, when started, continue until equilibrium conditions are reached.

The effect of curvature upon vapor pressure may be determined by thermodynamics, resulting in the relation

$$p = p_0 \left(1 + \frac{2\gamma M}{r d R T}\right) \quad (7)$$

where

- p_0 = normal vapor pressure
- p = vapor pressure of small drop
- γ = surface tension
- M = molecular weight
- d = density
- r = radius of drop
- R = gas constant
- T = absolute temperature

BOILING-POINT

When a liquid surface is exposed to a space in which the *total* gas pressure is less than the equilibrium vapor pressure of the liquid, a very rapid vaporization known as *boiling* takes place. Boiling results from the formation of tiny free spaces within the liquid itself. If the equilibrium vapor pressure is greater than the total pressure on the surface of the liquid, vaporization will take place in these free spaces which tend to form below the liquid surface. This vaporization will cause the formation of bubbles of vapor which crowd back the surrounding liquid and increase in size because of the greater pressure of the vapor. Such a bubble of vapor will rise to the surface of the liquid and join the main body of gas above it. Thus, when a liquid boils, vaporization takes place not only at the surface level but also at many interior surfaces of contact between the liquid and bubbles of vapor. The rising bubbles also break up the normal surface into more or less of a froth. The vapor once liberated from the liquid is at a higher pressure than the gas in which it finds itself and will immediately expand and flow away from the surface. These factors all contribute to make vaporization of a liquid relatively very rapid when boiling takes place. When the total pressure is such that boiling does not take place, vaporization will nevertheless continue, but at a slower rate, as long as the vapor pressure of the liquid exceeds the partial pressure of its vapor above the surface.

The temperature at which the equilibrium vapor pressure of a liquid equals the total pressure on the surface is known as the *boiling-point*. The boiling-point is entirely dependent on the total pressure, increasing with an increase in pressure. Theoretically, any liquid may be made to boil at any desired temperature by sufficiently altering the total pressure on its surface. Similarly, unless decomposition takes place, any liquid may be caused to boil at any desired pressure by sufficiently changing its temperature. The temperature at which a liquid boils when under a total pressure of 1.0 atmosphere is termed the *normal boiling-point*. This is the temperature at which the equilibrium vapor pressure equals 760 millimeters of mercury or 1.0 atmosphere.

VAPOR PRESSURES OF SOLIDS

Solid substances possess a tendency to disperse directly into the vapor state and to exert a vapor pressure just as do liquids. The transition of a solid directly into the gaseous state is termed *sublimation*, a process entirely analogous to the vaporization of a liquid. A familiar example of sublimation is the disappearance of snow in sub-zero weather.

Just as a liquid, a solid exerts an equilibrium vapor pressure which is a function of the nature of the material and the temperature. Sublimation will take place whenever the partial pressure of the vapor in contact with a solid surface is less than the equilibrium vapor pressure of the solid. Conversely, if the equilibrium vapor pressure of the solid is ex-

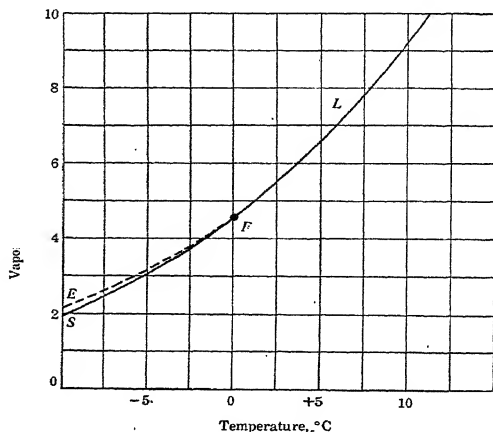


FIG. 8. Vapor Pressure of Water and Ice.

ceeded by the partial pressure of its vapor, condensation directly from the gaseous to the solid state will result.

At the melting-point the vapor pressures of a substance in the solid and liquid states are equal. At temperatures above the melting-point the solid state cannot exist. However, by careful cooling a liquid can be caused to exist in an unstable, supercooled state at temperatures below the melting-point. The vapor pressures of supercooled liquids are always greater than those of the solid state at the same temperature, and the liquid tends to change to the solid. The typical relationships between the vapor pressures of the solid and liquid states are illustrated in Fig. 8 for the case of water and ice. Point *F* is the melting-point.

Curve *FL* indicates the vapor pressures of the liquid, *FS* those of the solid, and *FE* those of the supercooled liquid.

The vapor pressures of solids, even at their melting-points, are generally small. However, in some cases these values become large and of considerable importance. For example, at its melting-point of 114.5° C iodine crystals exert a vapor pressure of 90 millimeters of mercury. Solid carbon dioxide at its melting-point of -56.7° C exerts a vapor pressure of 5.11 atmospheres and a pressure of 1.0 atmosphere at a temperature of -78.5° C. It is therefore impossible for liquid carbon dioxide to exist in a stable form at pressures less than 5.11 atmospheres.

Calculations dealing with the vapor pressures and sublimation of solids are entirely analogous to those of the vaporization of liquids. The principles and methods outlined in the following sections are equally applicable to sublimation and to vaporization processes.

VAPOR-GAS MIXTURES

When a gas or a gaseous mixture remains in contact with a liquid surface, it will acquire vapor from the liquid until the partial pressure of the vapor in the gas mixture equals the vapor pressure of the liquid at its existing temperature. When the vapor concentration reaches this equilibrium value the gas is said to be *saturated* with the vapor. It is not possible for the gas to contain a greater stable concentration of vapor, because, as soon as the vapor pressure of the liquid is exceeded by the partial pressure of the vapor, condensation takes place. The vapor content of a saturated gas is determined entirely by the vapor pressure of the liquid and may be predicted directly from vapor-pressure data.

The partial volume of the vapor in a saturated gas may be calculated from the relationships derived in Chapter III. Thus, if the simple gas law is applicable:

$$V_v = V \frac{p_v}{p} \quad (8)$$

where

V_v = partial volume of vapor

p_v = partial pressure of vapor = the vapor pressure of
the liquid at the existing temperature

V = total volume

p = total pressure

From Equation (8) the percentage composition by volume of a vapor-saturated gas may be calculated. The composition on a weight basis may be obtained from the composition by volume exactly as in the case of an ordinary gaseous mixture. When the simple gas law is applicable,

the composition by volume of a vapor-saturated gas is independent of the nature of the gas but is dependent on the nature and temperature of the liquid and on the total pressure. The composition by weight varies with the natures of both the gas and the liquid, the temperature, and the total pressure.

For certain types of engineering calculations it is convenient to use special methods of expression for the vapor content of a gas. The weight of vapor per unit volume of vapor-gas mixture, the weight of vapor per unit weight of vapor-free gas, and the mols of vapor per mol of vapor-free gas are three common and useful methods of expression. The number of mols of vapor per mol of vapor-free gas is the same as the partial volume of vapor per unit partial volume of vapor-free gas. When a gas is saturated with vapor, the composition expressed by the first method is independent of both the nature of the gas and the total pressure but varies with the nature and temperature of the liquid. When the composition is expressed by the third method it varies with the nature of the liquid, the temperature, and the pressure but is independent of the nature of the gas. From a knowledge of the equilibrium vapor pressure of the liquid the compositions of vapor-saturated gases may be readily calculated in any of these methods of expression, using the principles developed in Chapter III.

Illustration 5. Ethyl ether at a temperature of 20° C exerts a vapor pressure of 442 mm of Hg. Calculate the composition of a saturated mixture of nitrogen and ether vapor at a temperature of 20° C and a pressure of 745 mm of Hg expressed in the following terms:

- Percentage composition by volume.
- Percentage composition by weight.
- Pounds of vapor per cubic foot of mixture.
- Pounds of vapor per pound of vapor-free gas.
- Pound-mols of vapor per pound-mol of vapor-free gas.

a. Basis: 1.0 cu ft of mixture.

$$\text{Partial volume of vapor} = 1.0 \times \frac{442}{745} = \dots\dots\dots 0.593 \text{ cu ft}$$

Composition by volume:

Ether vapor.....	59.3%
Nitrogen.....	40.7%

b. Basis: 1.0 lb-mol of the mixture.

Vapor present = 0.593 lb-mol or.....	43.9 lb ✓
Nitrogen present = 0.407 lb-mol or.....	11.4 lb ✓
Total mixture.....	55.3 lb

Composition by weight:

Ether vapor.....	79.4%
Nitrogen.....	20.6%

c. *Basis:* Same as b.

$$\text{Volume} = 359 \times \frac{760}{745} \times \frac{293}{273} = \dots\dots\dots 393 \text{ cu ft}$$

$$\text{Weight of ether per cubic foot} = \frac{43.9}{393} = \dots\dots\dots 0.112 \text{ lb}$$

This result is independent of the total pressure. For example, an increase in the total pressure would decrease the volume per mol of mixture but would correspondingly decrease the weight of vapor per mol of mixture.

d. *Basis:* Same as b.

$$\text{Weight of vapor per pound nitrogen} = \frac{43.9}{11.4} = \dots\dots\dots 3.85 \text{ lb}$$

e. *Basis:* Same as b.

Mols of vapor per mol of nitrogen = $\frac{0.593}{0.407} = 1.455$ = the partial volume of ether per unit partial volume of nitrogen. This result is independent of the nature of the gas with which the ether vapor is mixed.

Partial Saturation. If a gas contains a vapor in such proportions that its partial pressure is less than the vapor pressure of the liquid at the existing temperature, the mixture is but partially saturated. The *relative saturation* of such a mixture may be defined as the percentage ratio of the partial pressure of the vapor to the vapor pressure of the liquid at the existing temperature. The relative saturation is therefore a function of both the composition of the mixture and its temperature as well as of the nature of the vapor.

From its definition it follows that the relative saturation also represents the following ratios:

a. The ratio of the percentage of vapor by volume to the percentage by volume which would be present were the gas saturated at the existing temperature and total pressure.

b. The ratio of the weight of vapor per unit volume of mixture to the weight per unit volume present at saturation at the existing temperature and total pressure.

Another useful means for expressing the degree of saturation of a vapor-bearing gas may be termed the *percentage saturation*. The percentage saturation is defined as the percentage ratio of the existing weight of vapor per unit weight of vapor-free gas to the weight of vapor which would exist per unit weight of vapor-free gas if the mixture were saturated at the existing temperature and pressure. The percentage saturation also represents the following ratios:

a. The ratio of the existing mols of vapor per mol of vapor-free gas to the mols of vapor which would be present per mol of vapor-free gas if the mixture were saturated at the existing temperature and pressure.

b. The ratio of the existing partial volume of vapor per unit partial volume of vapor-free gas to the partial volume of vapor which would exist per unit partial volume of vapor-free gas if the mixture were saturated at the existing temperature and pressure.

Care must be exercised that the *relative saturation* and the *percentage saturation* are not confused. They approach equality when the vapor concentrations are low.

Illustration 6. A mixture of acetone vapor and nitrogen contains 14.8% acetone by volume. Calculate the relative saturation and the percentage saturation of the mixture at a temperature of 20° C and a pressure of 745 mm of Hg.

The vapor pressure of acetone at 20° C is.....	184.8 mm of Hg
Partial pressure of acetone = 0.148×745 =	110 mm of Hg
Relative saturation = $110/184.8$ =	59.7%

Basis: 1.0 lb-mol of mixture.

Acetone.....	0.148 lb-mol
Nitrogen.....	0.852 lb-mol
Mols of acetone per mol of nitrogen = $0.148/0.852$ =	0.174

Basis: 1.0 lb-mol of saturated mixture at 20° C and 745 mm of Hg.

Percentage by volume of acetone = $184.8/745$ =	24.8%
Lb-mols of acetone =	0.248
Lb-mols of nitrogen =	0.752
Mols of acetone per mol of nitrogen = $0.248/0.752$ =	0.329
Percentage saturation = $0.174/0.329$ =	52.9%

As indicated by this illustration, the percentage saturation is always somewhat smaller than the relative saturation.

The composition of a partially saturated gas-vapor mixture is fixed if the relative or percentage saturation and the temperature and pressure are specified. From this information and a knowledge of the equilibrium vapor pressure at this temperature the composition may be expressed in any other terms. Conversely, the relative or percentage saturation may be calculated if the composition, pressure, and temperature are specified. The temperature required to produce a specified degree of saturation may be calculated if the composition at a specified pressure is known.

Illustration 7. A mixture of ethyl alcohol vapor and air has a relative saturation of 60% at a temperature of 40° C and a pressure of 740 mm of Hg. Calculate the percentage of vapor by volume and the mols of vapor per mol of vapor-free air.

The vapor pressure of alcohol at 40° C is given in the International Critical Tables as 135.3 mm of Hg.

$$\text{Partial pressure of alcohol} = 0.60 \times 135.3 = \dots\dots 81.2 \text{ mm}$$

Composition by volume:

Alcohol = $81.2/740$ =	11.0%
Air =	89.0%
Mols of alcohol per mol of air = $0.11/0.89$ =	0.124

Illustration 8. A mixture of ethyl alcohol and air has a percentage saturation of 60% at a temperature of 40° C and a pressure of 740 mm of Hg. Calculate the mols of vapor per mol of vapor-free air and the partial pressure of the vapor.

The vapor pressure of alcohol at 40° C is 135.3 mm of Hg.

Basis: 1.0 lb-mol of saturated mixture at 40° C and 740 mm of Hg.

Alcohol = $135.3/740 =$	0.183 lb-mol
Air =	0.817 lb-mol
Mols of vapor per mol of air = $0.183/0.817 =$	0.224

Basis: 1.0 lb-mol of air in the specified, unsaturated mixture.

Mols of vapor per mol of air = $0.224 \times 0.60 =$	0.134
Total gas =	1.134 lb-mols

Composition by volume = molal composition.

Alcohol = $0.134/1.134 =$	11.85%
Air =	88.15%
Partial pressure of alcohol = $0.1185 \times 740 =$	87.6 mm of Hg

Illustration 9. Moist air is found to contain 8.1 grains of water vapor per cubic foot at a temperature of 30° C. Calculate the temperature to which it must be heated in order that its relative saturation shall be 15%.

Basis: 1 cu ft of moist air.

Water = $\frac{8.1}{7000} = 1.16 \times 10^{-3}$ lb or	6.42×10^{-6} lb-mol
Partial volume of water vapor = $6.42 \times 10^{-6} \times 359 =$	0.0230 cu ft at S.C.
Partial pressure of water vapor = $760 \times \frac{0.0230}{1.0} \times \frac{303}{273} =$	19.4 mm of Hg
Vapor pressure of water at temperature corresponding to 15% relative saturation = $\frac{19.4}{0.15} =$	130 mm of Hg

From the vapor pressure data for water, Fig. 6, it is found that this pressure corresponds to a temperature of 57° C.

Humidity. Because of the widespread occurrence of water vapor in gases of all kinds, special attention has been given to this case and a special terminology has been developed. The *humidity* of a gas is generally defined as the weight of water per unit weight of moisture-free gas. The *molal humidity* is the number of mols of water per mol of moisture-free gas. When the vapor under consideration is water the percentage saturation is termed the *percentage humidity*. The relative saturation becomes the *relative humidity*.

Considerable confusion exists in the literature in the use of these terms, and care must always be exercised to avoid misuse. The terminology recommended above is an extension of that proposed by Grosvenor.¹

The Dew-Point. If an unsaturated mixture of vapor and gas is cooled, the relative amounts of the components and the percentage composition

¹ Trans. Am. Inst. Chem. Eng. 1 (1908).

by volume will at first remain unchanged. It follows that, if the total pressure is constant, the partial pressure of the vapor will be unchanged by the cooling. This will be the case until the temperature is lowered to such a value that the vapor pressure of the liquid at this temperature is equal to the existing partial pressure of the vapor in the mixture. The mixture will then be saturated, and any further cooling will result in condensation. The temperature at which the equilibrium vapor pressure of the liquid is equal to the existing partial pressure of the vapor is termed the *dew-point* of the mixture.

The dew-point of a gas-vapor mixture may be experimentally determined by introducing into it a polished surface which may be cooled to any desired temperature. By gradually cooling such a surface below the temperature of the gas, the dew-point may be detected as the temperature at which the polished surface is first clouded by a film of condensate. The vapor pressure of the liquid at this temperature is equal to the partial pressure of the vapor in the gas mixture. Measurement of the dew-point constitutes a rapid and accurate method for determining the concentration of any vapor when present alone in a gas mixture which is not too far distant from saturation. At saturation the dew-point is equal to the existing temperature of the gas. As the mixture becomes less saturated the dew-point becomes lower and lower.

The vapor content of a vapor-gas mixture may be calculated from dew-point data, or conversely, the dew-point may be predicted from the composition of the mixture.

Illustration 10. Ether vapor is mixed with nitrogen at a temperature of 30° C and a pressure of 750 mm of Hg. The dew-point of the mixture is 20° C.

- Calculate the partial pressure of the ether.
- Calculate the composition by volume of the mixture.
- Calculate the relative saturation of the mixture.
- Calculate the mols of vapor per mol of vapor-free nitrogen.

The vapor pressure of ether is listed in the International Critical Tables as 647.3 mm of Hg at 30° C and 442.2 mm of Hg at 20° C.

Solution:

- Partial pressure of vapor = 442.2 mm of Hg
- Composition by volume:

Ether = $442.2/750 =$	59%
Nitrogen =	41%

- Relative saturation = $442.2/647.3 =$ 68.4%
- Basis:* 1.0 lb-mol.

Ether =	0.59 lb-mol
Nitrogen =	0.41 lb-mol

$$\text{Mols of ether per mol of nitrogen} = \frac{0.59}{0.41} = \dots\dots\dots 1.44$$

Illustration 11. A mixture of benzol vapor and air contains 10.1% benzol by volume.

- Calculate the dew-point of the mixture when at a temperature of 25° C and a pressure of 750 mm of Hg.
- Calculate the dew-point when the mixture is at a temperature of 30° C and a pressure of 750 mm of Hg.
- Calculate the dew-point when the mixture is at a temperature of 30° C and a pressure of 700 mm of Hg.

Solution:

- Partial pressure of benzol = $0.101 \times 750 = \dots\dots\dots$ 75.7 mm Hg
From the vapor pressure data for benzol, Fig. 3, it is found that this pressure corresponds to a temperature of 20.0° C, the dew-point.
- Partial pressure of benzol = $\dots\dots\dots$ 75.7 mm
Dew-point = $\dots\dots\dots$ 20.0° C
- Partial pressure of benzol = $0.101 \times 700 = \dots\dots\dots$ 70.7 mm Hg

The temperature corresponding to a vapor pressure of 70.7 mm of Hg is found to be 18.7° C. From these results it is seen that the dew-point does not depend on the temperature but does vary with the total pressure.

VAPORIZATION PROCESSES

The manufacturing processes of drying, air-conditioning and certain types of evaporation all involve the vaporization of a liquid into a stream of gases. In dealing with such processes it is of interest to calculate the relationships between the quantities and volumes of gases entering and leaving and the quantity of material evaporated. Such problems are of the general class which was discussed in Chapter III under the heading of "Volume Changes with Change in Composition." The concentrations of vapor in these problems are generally expressed in terms of the dew-points, the relative saturations, or the mols of vapor per mol of vapor-free gas. The first two methods of expression are convenient because they are directly determined from dew-point or wet- and dry-bulb temperature measurements. From such data the partial pressures of vapor may be readily calculated and the partial pressure method of solution might be used as described in Chapter III.

The vaporization processes all require the introduction of energy in the form of heat. The effective utilization of this heat is frequently the most important factor governing the operation of the process, and a knowledge of the relationships between the quantity of heat introduced and that dissipated in various ways is of great significance. The calculation of such a *heat balance* is greatly simplified if the quantities of all materials concerned are expressed in molal or weight units rather than in volumes. These units have the advantage of expressing quantity independent of change of temperature and pressure. The same desirability of weight or molal units arises when relationships are derived for

the design of vaporization equipment. For these reasons it has become customary to express all data in either weight or molal units where thermal calculations are to be made or where design relationships are to be used. The molal units are preferable. From data expressed in molal units, volumes at any desired conditions may be readily obtained. In thermal calculations considerable simplification results from the fact that the thermal properties per mol of many materials are similar or related.

Results of vaporization calculations are obtained most directly if all vapor concentrations are expressed in molal or weight units which are based on fixed quantities of the inactive permanent gas which passes through the process without change in quantity. The mols of vapor per mol of vapor-free gas or the weight of vapor per unit weight of vapor-free gas are the most useful units of this type. When such units are used for expression of concentrations, the labor of calculating the relationships between all the quantities of materials and heat in the process is reduced to a minimum. Concentrations in terms of partial pressures are easily converted to these units. By the use of the *humidity chart*, which will be discussed later, concentrations in special cases may be determined directly in these units from wet- and dry-bulb temperature measurements. It is recommended that *in all vaporization and condensation calculations the vapor concentrations be expressed in mols of vapor per mol of vapor-free gas*. The same method may be used profitably for expression of the concentrations of the solute gas in gas absorption processes.

It will be noted that in any mixture following the simple gas law the ratio of the number of mols of vapor to the number of mols of vapor-free gas is equal to the ratio of the partial pressure of the vapor to the partial pressure of the vapor-free gas. Accordingly, vapor concentration in mols of vapor per mol of vapor-free gas is obtained by dividing the partial pressure of the vapor by the partial pressure of the vapor-free gas.

Illustration 12. It is proposed to recover acetone, which is used as a solvent in an extraction process, by evaporation into a stream of nitrogen. The nitrogen enters the evaporator at a temperature of 30° C containing acetone such that its dew-point is 10° C. It leaves at a temperature of 25° C with a dew-point of 20° C. The barometric pressure is constant at 750 mm of Hg.

a. Calculate the vapor concentrations of the gases entering and leaving the evaporator, expressed in mols of vapor per mol of vapor-free gas.

b. Calculate the mols of acetone evaporated per mol of vapor-free gas passing through the evaporator.

c. Calculate the weight of acetone evaporated per 1000 cu ft of gases entering the evaporator.

d. Calculate the volume of gases leaving the evaporator per 1000 cu ft entering it

Solution: From Figs. 5 and 6, the vapor pressure of acetone is:

116 mm of Hg at 10° C.

185 mm of Hg at 20° C

a. Entering gases:

Partial pressure of acetone = 116 mm of Hg

Partial pressure of nitrogen = 750 - 116 = 634 mm of Hg

Mols of acetone per mol of nitrogen = 116/634 = 0.183

Leaving gases:

Partial pressure of acetone = 185 mm of Hg

Partial pressure of nitrogen = 750 - 185 = 565 mm of Hg

Mols of acetone per mol of nitrogen = 185/565 = 0.328

b. Basis: 1.0 lb-mol of nitrogen.

Acetone leaving the process = 0.328 lb-mol

Acetone entering the process = 0.183 lb-mol

Acetone evaporated 0.145 lb-mol

c. Basis: 1.0 lb-mol of nitrogen.

Total gas entering the process = 1.0 + 0.183 = 1.183 lb-mols

Volume of gas entering = $1.183 \times 359 \times \frac{760}{750} \times \frac{303}{273} = \dots$ 477 cu ft

Molecular weight of acetone = 58

Weight of acetone evaporated = $58 \times 0.145 = \dots$ 8.4 lb

Acetone evaporated per 1000 cu ft of gas entering =

$\frac{8.4}{477} \times 1000 = \dots$ 17.6 lb

d. Basis: 1.0 lb-mol of nitrogen.

Total gas leaving the process = 1.0 + 0.328 = 1.328 lb-mols

Volume of gas leaving = $1.328 \times 359 \times \frac{760}{750} \times \frac{298}{273} = \dots$ 526 cu ft

Volume of gas leaving per 1000 cu ft entering the process

$= \frac{526}{477} \times 1000 = \dots$ 1102 cu ft

Illustration 13. Air enters a drier at a temperature of 195° F with a molal humidity of 0.029. It is found that 1.4 lb of water are evaporated in the drier per 1000 cu ft of air entering. The air leaves the drier at a temperature of 102° F. The entire process is at the normal barometric pressure of 760 mm of Hg.

Calculate the molal humidity and percentage humidity of the air leaving the drier.

Basis: 1000 cu ft of wet air entering the drier.

Mols of wet air = $\frac{1000}{359 \times \frac{655}{492}} = \dots$ 2.09 lb-mols

Water entering = $2.09 \times \frac{0.029}{1.029} = \dots$ 0.059 lb-mol

Dry air entering = 2.03 lb-mols

Water leaving = $0.059 + \frac{1.4}{18} = \dots$ 0.137 lb-mol

$$\begin{aligned}
 \text{Molal humidity of air leaving} &= \frac{0.137}{2.03} = \dots\dots\dots 0.0675 \\
 \text{Vapor pressure of water at } 102^\circ \text{ F} &= \dots\dots\dots 52.2 \text{ mm of Hg} \\
 \text{Molal humidity of air leaving if it were saturated} &= \\
 \frac{52.2}{760 - 52.2} &= \dots\dots\dots 0.0737 \\
 \text{Percentage humidity of air leaving} &= \frac{0.0675}{0.0737} = \dots\dots\dots 91.5\%
 \end{aligned}$$

CONDENSATION

The relative saturation of a partially saturated mixture of vapor and gas may be increased in two ways without the introduction of additional vapor. If the temperature of the mixture is reduced, the vapor concentration corresponding to saturation is reduced, thereby increasing the relative saturation even though the existing partial pressure of the vapor is unchanged. If the total pressure is increased the existing partial pressure of the vapor is increased, again increasing the relative saturation. Thus, by sufficiently increasing the pressure or reducing the temperature of a vapor-gas mixture it is possible to cause it to become saturated, the existing partial pressure of vapor equaling the vapor pressure of the liquid at the existing temperature. Further reduction of the temperature or increase of the pressure will result in condensation, since the partial pressure of the vapor cannot exceed the vapor pressure of the liquid in a stable system.

In problems dealing with condensation processes, four interdependent factors are to be considered: the initial composition, the final temperature, the final pressure, and the quantity of condensate. It may be desired to calculate any one of these factors when the others are known or specified. Such calculations are readily carried out by selecting as a basis a definite quantity of vapor-free gas and calculating the quantities of vapor which are associated with it at the various stages of the process. In a condensation process the final conditions will be those of saturation at the final temperature and pressure. Any one of the three methods of calculation demonstrated in Chapter III under "Volume Changes with Change in Composition" may be used. However, for the reasons given in the preceding section it is generally desirable to express the vapor concentrations in mols of vapor per mol of vapor-free gas if any thermal or design calculations are to be carried out.

Illustration 14. Air at a temperature of 20° C and a pressure of 750 mm of Hg has a relative humidity of 80%.

a. Calculate the molal humidity of the air.

b. Calculate the molal humidity of this air if its temperature is reduced to 10° C and its pressure increased to 35 lb per sq in., condensing out some of the water.

- c. Calculate the weight of water condensed from 1000 cu ft of the original wet air in cooling and compressing to the conditions of part b.
 d. Calculate the final volume of the wet air of part c.

Vapor pressure of water:

17.5 mm of Hg at 20° C

9.2 mm of Hg at 10° C

Solution:

- a. Initial partial pressure of water = $0.80 \times 17.5 = \dots$ 14.0 mm of Hg
 Initial molal humidity = $\frac{14.0}{750 - 14.0} = \dots$ 0.0190
 b. Final partial pressure of water = \dots 9.2 mm of Hg
 Final total pressure = $35 \times \frac{760}{14.7} = \dots$ 1810 mm of Hg
 Final molal humidity = $\frac{9.2}{1810 - 9.2} = \dots$ 0.0051

Basis: 1000 cu ft of original wet air.

- c. Partial pressure of dry air = $750 - 14 = \dots$ 736 mm of Hg
 Partial volume of dry air at S.C. = $1000 \times \frac{736}{760} \times \frac{273}{293} = \dots$ 903 cu ft
 Mols of dry air = $903/359 = \dots$ 2.52 lb-mols
 Water originally present = $2.52 \times 0.0190 = \dots$ 0.0478 lb-mol
 Water finally present = $2.52 \times 0.0051 = \dots$ 0.0128
 Water condensed = 0.0350 lb-mol or = \dots 0.630 lb
 d. Total wet air finally present = $2.52 + 0.0128 = \dots$ 2.53 lb-mols
 Final volume of wet air = $2.53 \times 359 \times \frac{760}{1810} \times \frac{283}{273} = \dots$ 396 cu ft

Illustration 15. A mixture of dry flue gases and acetone at a pressure of 750 mm of Hg and a temperature of 30° C has a dew-point of 25° C. It is proposed to condense 90% of the acetone in this mixture by cooling to 5° C and compressing. Calculate the necessary pressure in pounds per square inch.

Vapor pressure of acetone:

at 30° C = 282.7 mm of Hg

at 25° C = 229.2 mm of Hg

at 5° C = 89.1 mm of Hg

Solution:

Basis: 1.0 lb-mol of original mixture.

- Partial pressure of acetone = \dots 229.2 mm of Hg
 Acetone present = $229.2/750 = \dots$ 0.306 lb-mol
 Flue gases present = \dots 0.694 lb-mol
 Acetone present in final mixture = $0.10 \times 0.306 = \dots$ 0.0306 lb-mol
 Final mixture of gas = $0.694 + 0.0306 = \dots$ 0.725 lb-mol
 Partial pressure of acetone in final mixture = \dots 89.1 mm
 (the vapor pressure at 5° C)
 Mol percentage of acetone in final mixture = \dots
 $0.0306/0.725 = \dots$ 4.22%
 Final pressure = $\frac{89.1}{0.0422} = \dots$ 2110 mm of Hg or \dots 40.8 lb per sq in

Illustration 16. A mixture of carbon tetrachloride (CCl_4) and air has a relative saturation of 70% at a temperature of 60°C and a pressure of 745 mm of Hg.

a. Calculate the temperature to which this mixture must be cooled in order to condense 80% of the vapor present.

b. Calculate the weight of vapor condensed from 1000 cu ft of the original mixture.

c. Calculate the volume of mixture remaining after cooling 1000 cu ft of the original mixture.

Vapor pressure of CCl_4 at 60°C = 450.8 mm of Hg

Solution:

Basis: 1.0 lb-mol of the original mixture.

a. Partial pressure of vapor = $0.70 \times 450.8 = \dots\dots\dots$ 316 mm of Hg

Mols of vapor = $316/745 = \dots\dots\dots$ 0.424 lb-mol

Mols of air = 0.576 lb-mol

Vapor in final mixture = $0.20 \times 0.424 = \dots\dots\dots$ 0.0848 lb-mol

Total final mixture = $0.0848 + 0.576 = \dots\dots\dots$ 0.661 lb-mol

Partial pressure of CCl_4 in final mixture =

745 = 96 mm of Hg

A vapor pressure of 96 mm of Hg for carbon tetrachloride corresponds to a temperature of 21°C , the temperature to which the mixture must be cooled.

CCl_4 condensed = $0.424 - 0.0848 = 0.339$ lb-mol or $0.339 \times 154 = \dots\dots\dots$ 52.2 lb

b. Volume of original mixture = $359 \times \frac{760}{745} \times \frac{333}{273} = \dots\dots\dots$ 447 cu ft

Weight of CCl_4 condensed from 1000 cu ft of original mixture

= $\frac{52.2}{447} \times 1000 = \dots\dots\dots$ 117 lb

Volume of final mixture = $0.661 \times 359 \times \frac{294}{273} \times \frac{760}{745} = \dots\dots\dots$ 261 cu ft

c. Volume of final mixture per 1000 cu ft of original mixture =

$\frac{261}{447} \times 1000 = \dots\dots\dots$ 584 cu ft

Illustration 17. A mixture of normal pentane and dry water-gas has a percentage saturation of 20% at a temperature of 70°F and a pressure of 760 mm of Hg. For distribution this gas is compressed to a gauge pressure of 35 lb per sq in. Calculate the weight of pentane condensed from 1 pound-mol of the original mixture if the temperature in the mains falls to -20°F .

Vapor pressures of pentane:

at 70°F = 440 mm of Hg

at -20°F = 42 mm of H

Solution:

Initial mixture:

Mols of pentane per mol of water-gas:

$\frac{440}{760 - 440} \times 0.20 = \dots\dots\dots$ 0.275

Final mixture:

$$\begin{aligned}\text{Total pressure} &= (35 + 14.7) \frac{760}{14.7} = \dots\dots\dots 2570 \text{ mm Hg} \\ \text{Mols of pentane per mol of water-gas} &= \\ \frac{42}{2570 - 42} &= \dots\dots\dots 0.0166\end{aligned}$$

Basis: 1.0 lb-mol of original mixture:

$$\begin{aligned}\text{Pentane} &= \frac{0.275}{1.275} = \dots\dots\dots 0.216 \text{ lb-mol} \\ \text{Water-gas} &= \dots\dots\dots 0.784 \text{ lb-mol} \\ \text{Pentane in final mixture} &= 0.784 \times 0.0166 = \dots\dots\dots 0.0130 \text{ lb-mol} \\ \text{Pentane condensed} &= 0.216 - 0.0130 = 0.203 \text{ lb-} \\ &\text{mol or } 0.203 \times 72 = \dots\dots\dots 14.6 \text{ lb}\end{aligned}$$

WET- AND DRY-BULB THERMOMETRY

When a liquid evaporates into a large volume of gas at the same temperature, if no heat is supplied from an external source the liquid will be cooled as a result of the heat abstracted from it to supply the relatively large demand of the latent heat of vaporization. If the body of liquid has a large surface area in proportion to its mass, its temperature will quickly drop to an equilibrium value. This equilibrium temperature which is assumed by the evaporating liquid will be such that heat will be transferred to it from the warmer gas at a rate which is just adequate to supply the necessary latent heat for the vaporization. The equilibrium temperature of a liquid when vaporizing into a gas is termed the *wet-bulb* temperature and is always less than the actual *dry-bulb* temperature of the gas into which evaporation is taking place. If the gas is saturated there is neither vaporization nor depression of the wet-bulb temperature. It is therefore possible to use the depression of the wet-bulb temperature as a measure of the degree of unsaturation of the mixture of gas and vapor.

The wet-bulb temperature of a vapor-bearing gas may easily be determined by covering the bulb of a thermometer with a wick which is saturated with the liquid. This wet-bulb thermometer is inserted into the gas mixture. In order to prevent local increases in vapor concentration the wet bulb must be ventilated, either by moving it through the gas or by blowing the gas over it. It has been experimentally demonstrated that the extent of ventilation has no effect on the wet-bulb depression when a certain minimum ventilation is exceeded. When ventilation is not rapid care must be taken that the thermometer does not gain heat from its surroundings by radiation.

The principles of wet- and dry-bulb thermometry may be applied to determination of the vapor concentrations in a great variety of systems

of liquids and gases. Thus, the concentration of benzol in a mixture of benzol vapor and dry air might be determined by measuring the depression in it of a wet-bulb thermometer the wick of which is saturated with benzol. Similarly, to determine the humidity of a gas a wet-bulb thermometer is used which is saturated with water. However, before wet- and dry-bulb thermometer data may be conveniently translated into the corresponding vapor concentrations, rather elaborate charts or tables must be worked out to express vapor concentrations in terms of wet- and dry-bulb temperatures. Sufficient data are available for the evaluation of such charts for many systems of liquids and gases by a method which is discussed in Chapter V, page 148.

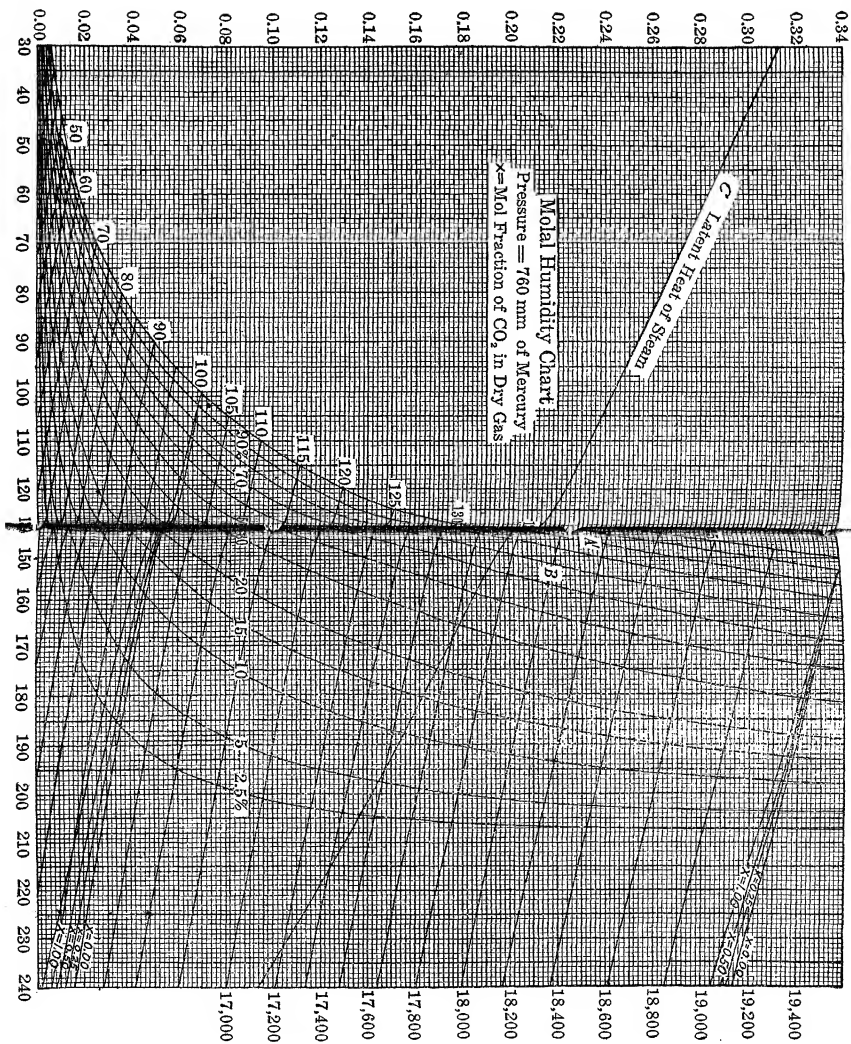
Although, by the evaluation of the required equations or charts, it is possible to extend wet- and dry-bulb thermometry to the determination of concentrations of different types of vapors, the only systems for which the method has been extensively used are those involving water vapor. This special application of wet- and dry-bulb thermometry is termed *hygrometry* or *psychrometry*. The United States Weather Bureau has worked out extensive psychrometric tables and charts from which humidities of air may be obtained with very satisfactory accuracy. For engineering purposes *humidity charts* have been developed which permit the determination of the humidities of any of the common gases from wet- and dry-bulb thermometric data. The limitation of these charts is that *each chart is applicable only to systems which exist under a single, specified total pressure*. For other total pressures it is necessary to develop other charts. The humidity charts are very useful for rapid solutions of many of the problems of vaporization, condensation, and air-conditioning processes which occur at substantially constant atmospheric pressure.

Charts exactly similar to the humidity charts may be calculated for other systems of liquids and gases from existing data. The construction of such charts is justified only where a considerable amount of attention is to be devoted to a single system.

The Humidity Chart. In Fig. 9 is plotted a molal humidity chart covering a range of molal humidities from 0.00 to 0.34, and a range of dry-bulb temperatures from 30° to 250° F. A chart of this type was described in the literature by Hatta.¹ A lower range on a semi-log scale is shown in Fig. 10. Values of molal humidities are plotted as ordinates and dry-bulb temperatures as abscissas. The chart is based on a total pressure of 1.0 atmosphere. Included on the same chart is curve *C* showing the relationship between the molal heat of vaporization of water as ordinates and temperature as abscissas.

¹ Chem. and Met. Eng. 37, 137 (1930).

Molal Humidity



Molal Latent Heat, Btu per lb-mol

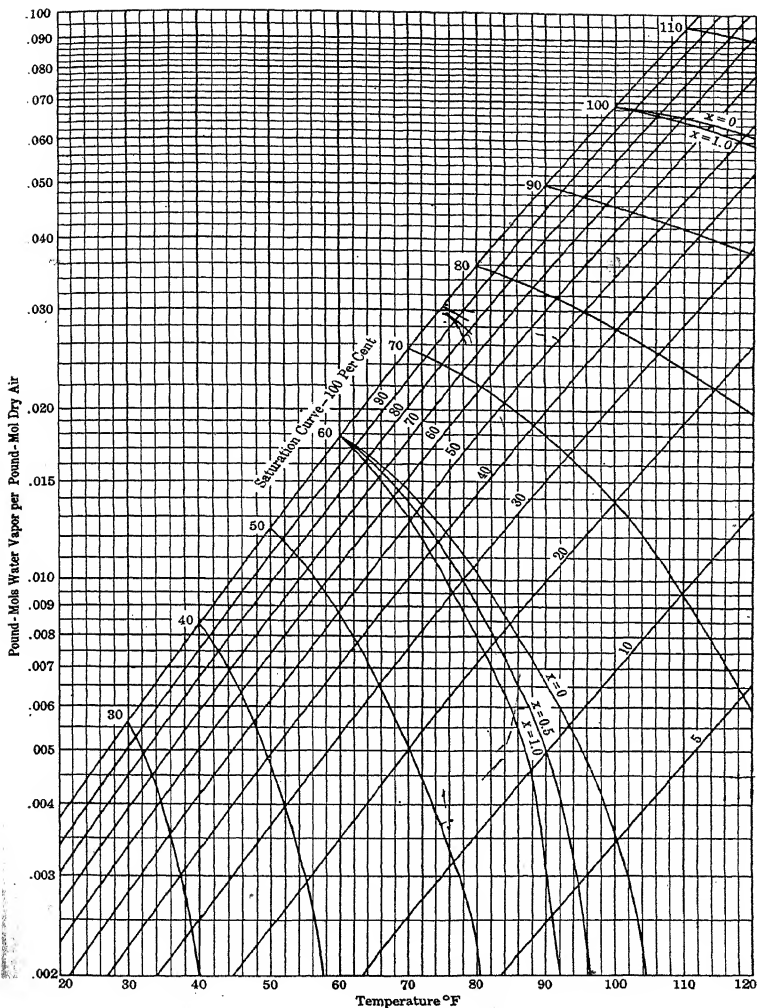


FIG. 10. Molal Humidity Chart. Low Temperature Range.

Pressure = 1 atmosphere = 29.92 in. of mercury.

x = mol fraction of CO_2 in dry gas.

(To use either Fig. 9 or 10 in obtaining the pounds of water per pound of dry air multiply molal humidity, ordinates of the charts, by 18/29 or 0.62.)

Curve *A* of Fig. 9, termed the saturation curve, is a plot of molal humidity against temperature for any gas which is saturated with water vapor. Curves *A'* express similar relationships between molal humidities and temperatures corresponding to the specified values of *percentage* humidity less than unity. These curves are all independent of the nature of the gas under consideration.

Curves *B* are lines of constant wet-bulb temperature when the gas is composed of only diatomic components such as oxygen, nitrogen, carbon monoxide, hydrogen, and the like. One of these curves indicates the wet-bulb temperature of any mixture whose dry-bulb temperature and molal humidity determine a point falling on this curve. By interpolation between these curves it is possible to estimate any one of the properties of molal humidity, wet-bulb temperature, and dry-bulb temperature if the other two are known. It will be noted that where the wet-bulb temperature lines cross the saturation curve *A* the wet-bulb temperature must be equal to the dry-bulb temperature.

At wet-bulb temperatures of 100° and 150° F are groups of curves which indicate the effect on the wet-bulb temperature lines of the presence of triatomic gases such as carbon dioxide. The symbol x indicates the mol fraction of triatomic gases in the *dry* gas mixture. All wet-bulb lines on the chart for which no value of x is designated correspond to a composition of $x = 0$. The wet-bulb temperature lines which correspond to various mixtures of gases must converge at the saturation curve where the wet-bulb temperature is equal to the dry-bulb, regardless of the dry gas composition. These lines permit application of the chart to mixtures of the common gases. For example, the wet- and dry-bulb temperatures of a mixture of composition x' are known. These temperature data approximately locate the point on the chart representing the conditions of the mixture. From the nearest family of x -curves the angle between the lines $x = 0$ and $x = x'$ is estimated. Any wet-bulb temperature line for the mixture x' may now be determined by establishing a line from the wet-bulb temperature on the saturation curve *A* at this same angle to the nearest wet-bulb line which corresponds to a composition of $x = 0$. This method of interpolation is satisfactory because the wet-bulb temperature lines of a mixture of any designated composition are approximately straight lines whose slopes do not vary greatly.

A line on the chart which is parallel to the temperature axis represents a change of temperature without change in molal humidity. This fact may be used for estimation of the dew-point of a mixture whose properties are represented by an established point on the chart. A line is projected through this point, parallel to the temperature axis, to the satura-

tion curve *A*. The abscissa of the intersection of this line with the saturation curve is the dew-point of the mixture.

The use of the chart is demonstrated in the following illustrations:

Illustration 18. Air at a temperature of 100° F and atmospheric pressure has a wet-bulb temperature of 85° F.

a. Estimate the molal humidity, the percentage saturation, and the dew-point of this air.

b. The air of part *a* is passed into an evaporator from which it emerges at a temperature of 120° F with a wet-bulb temperature of 115.3° F. Estimate the percentage saturation of the air leaving the evaporator and calculate the weight of water evaporated per 1000 cu ft of entering air.

Solution: *a.* The abscissa representing 100° F is located on Fig. 10 and followed vertically to its intersection with the 85° F wet-bulb temperature line. This point represents the initial conditions of the air. The percentage saturation is estimated from the position of this point with respect to the curves corresponding to various degrees of saturation. This value would be estimated to be about 52%. The molal humidity is read from the scale of ordinates as 0.037. The dew-point is determined by following a horizontal line to its intersection with the saturation curve. The abscissa of this point of intersection is 80.5° F, the dew-point.

b. In the manner described above the percentage saturation of the air leaving the evaporator is estimated to be 84% and its molal humidity 0.110.

Basis: 1.0 lb-mol of moisture-free air.

$$\text{Mols of wet air entering} = 1.0 + 0.037 = \dots\dots\dots 1.037 \text{ lb-mol}^{\text{air}}$$

$$\text{Volume of wet air entering} = 1.037 \times 359 \times \frac{560}{492} = \dots\dots\dots 424 \text{ cu ft}$$

$$\text{Water evaporated} = 0.110 - 0.037 = 0.073 \text{ lb-mol or} = \dots\dots\dots 1.31 \text{ lb}$$

$$\text{Water evaporated per 1000 cu ft of entering wet air} = \frac{1000}{424} = \dots\dots\dots 3.1 \text{ lb}$$

Illustration 19. A combustion gas has the following composition:

CO ₂	12.1%
CO	0.1%
O ₂	7.6%
N ₂	80.2%
	<hr/> 100.0%

a. Estimate the wet-bulb temperature of this gas when moisture-free at a temperature of 200° F and atmospheric pressure.

b. If the combustion gas has a dry-bulb temperature of 140° F and a wet-bulb temperature of 95° F estimate its molal humidity.

Solution: *a.* From the group of *x*-curves corresponding to a wet-bulb temperature of 100° F, the angle between the curves for *x* = 0 and *x* = 0.12 is estimated. A line is established at this angle to the 85° wet-bulb line, which is closest to the point representing the conditions of the gas. A line parallel to this newly established 85° wet-bulb line, which corresponds to a composition *x* = 0.12, is projected from the point representing zero humidity and a dry-bulb temperature of 200° F. This line intersects with the saturation curve at a temperature of 87° F, which is the wet-bulb

temperature. These projections may be carried out with the aid of two draftsman's

b. In the manner described above, the angle between the curve $x = 0$ and $x = 0.12$ at a wet-bulb temperature of 100° is estimated. A line is established at this angle to the 95° wet-bulb line determining the 95° wet-bulb line corresponding to $x = 0.12$. The intersection of this line with the 140° dry-bulb temperature line establishes the point representing the conditions of the mixture. The ordinate of this point is 0.040, the molal humidity of the mixture.

If many calculations are to be made for a gas having an approximately constant value of x , it will be convenient to rule wet-bulb lines corresponding to this composition directly onto the chart. These lines can be established in the manner described above.

Adiabatic Vaporization. An adiabatic system or process is one which is completely prevented from either gaining heat from, or losing heat to its surroundings. Frequently the vaporization of a liquid into a gas will be of this type. As previously explained, the temperature of the vaporizing liquid will adjust itself to the wet-bulb value which is determined by the vapor content and temperature of the gas. As vaporization proceeds the vapor content of the gas is increased. However, it has been experimentally demonstrated that the wet-bulb temperature remains unchanged throughout such an adiabatic vaporization. The heat which is required for the vaporization of the liquid must be derived from the gas, reducing its temperature. If such a process is continued until the gas becomes saturated, the dry-bulb temperature of the gas will equal its wet-bulb temperature, which will be the same as its initial wet-bulb temperature. On the humidity chart the changes in humidity and dry-bulb temperature which take place in an adiabatic vaporization process are represented by a line of constant wet-bulb temperature. These wet-bulb temperature lines are also termed adiabatic vaporization or *adiabatic cooling* lines.

For example, from Fig. 9 it is seen that dry air at a temperature of 197° F has a wet-bulb temperature of 85° F. Suppose that dry air at this temperature is brought in contact, in an adiabatic compartment, with water at a temperature of 85° F. As vaporization takes place the molal humidity of the air will increase, but if its wet-bulb temperature is to remain constant the dry-bulb temperature must correspondingly decrease along the 85° F wet-bulb temperature line. Thus, if vaporization continues until the molal humidity of the air becomes 0.020 the dry-bulb temperature of the air will be reduced to 144° F. If the vaporization is continued until the air is saturated, the molal humidity will then be 0.042 and the dry-bulb temperature will be 85° F. This molal humidity of 0.042 represents the maximum quantity of water which can be adiabatically evaporated into dry air at an initial temperature of 197° F.

Many types of industrial equipment for drying and evaporation are practically adiabatic in operation, the heat for the vaporization being almost entirely abstracted from the hot gases which enter the process. The humidity chart permits rapid calculation of the quantities of water which can be evaporated in such processes and of the temperatures and humidities throughout.

Illustration 20. Air enters a drier at atmospheric pressure, a dry-bulb temperature of 190° F, and a wet-bulb temperature of 90° F. It is found that 0.028 lb-mol of water is evaporated in the drier per pound-mol of dry air entering it. Assuming that the vaporization is adiabatic, estimate the dry-bulb temperature, the wet-bulb temperature, and the percentage saturation of the air leaving the drier.

Solution: On Fig. 9 it is found that a dry-bulb temperature of 190° and a wet-bulb temperature of 90° correspond to a molal humidity of 0.011.

Molal humidity of air leaving = $0.011 + 0.028 = 0.039$.

If the process is adiabatic the wet-bulb temperature will remain constant at 90° F. A wet-bulb temperature of 90° and a molal humidity of 0.039 correspond to a dry-bulb temperature of 116° F, the temperature of the air leaving the drier. The percentage saturation is estimated as 35%.

Illustration 21. Carbon dioxide is saturated with water vapor by passing it through a wetted chamber. The gas enters the chamber dry, at atmospheric pressure, and at a temperature of 120° F. It may be assumed that the vaporization in the saturator is adiabatic. Estimate the temperature and molal humidity of the saturated carbon dioxide leaving the chamber.

Solution: For pure carbon dioxide, wet-bulb curves corresponding to $x = 1.0$ must be used. In the group of 100° wet-bulb curves the angle is determined between the curves $x = 0$ and $x = 1.0$. A line is established at this angle to the 65° wet-bulb line, thus determining the 65° wet-bulb line for $x = 1.0$. A line parallel to this is projected from the point representing a dry-bulb temperature of 120° and zero humidity to the saturation curve. The intersection is at a temperature of 71° F, the wet-bulb temperature. The molal humidity at this point is 0.027.

PROBLEMS

Solve the first 22 problems without the use of the humidity charts.

- 1a. Obtaining the necessary data from a physical table, preferably the International Critical Tables, plot a curve relating the vapor pressure of acetic acid ($C_2H_4O_2$) in millimeters of Hg to temperature in degrees Centigrade. Plot the curve for the temperature range from 20° to 140° C, using vapor pressures as ordinates and temperatures as abscissas, both on uniform scales.
- b. Ethylene glycol ($OHCH_2 \cdot CH_2OH$) has a normal boiling-point of 197° C. At a temperature of 120° C it exerts a vapor pressure of 39 mm of Hg. From these data construct a Dühring line for ethylene glycol using water as the reference substance. From this line and Fig. 6 estimate the vapor pressure at 160° C and the boiling-point under a pressure of 100 mm of Hg.
- c. Ethyl bromide (C_2H_5Br) exerts a vapor pressure of 165 mm of Hg at 0° C and has a normal boiling-point of 38.4° C. From Fig. 3 estimate its vapor pressure at 60° C.
- d. Nonane (C_9H_{20}) has a normal boiling-point of 150.6° C. From Fig. 4 estimate its boiling-point under a pressure of 100 mm of Hg.

- 2a. Calculate the composition, by volume and by weight, of air which is saturated with water vapor at a pressure of 750 mm of Hg and a temperature of 70° F.
 - b. Calculate the composition by volume and by weight of carbon dioxide which is saturated with water vapor at the conditions of part a. (The necessary data may be obtained from Fig. 6.)
 - 3a. Calculate the composition by volume and by weight of air which is saturated with benzol vapor at a pressure of 750 mm of Hg and a temperature of 70° F.
 - b. Calculate the composition, by volume and by weight, of carbon dioxide which is saturated with benzol vapor at the conditions of part a.
 4. Nitrogen is saturated with benzol vapor at a temperature of 25° C and a pressure of 750 mm of Hg. Calculate the composition of the mixture, expressed in the following terms:
 - a. Percentage by volume.
 - b. Percentage by weight.
 - c. Grains of benzol per cubic foot of mixture.
 - d. Pounds of benzol per pound of nitrogen.
 - e. Pound-mols of benzol per pound-mol of nitrogen.
 5. Benzol vapor is mixed with a permanent gas at a temperature of 27° C in such proportions that the partial pressure of the vapor is 60 mm of Hg.

Calculate: (1) the relative saturation; (2) the mols of benzol per mol of vapor-free gas; (3) the weight of benzol per unit weight of vapor-free gas; (4) the percentage saturation; (5) the percentage of benzol by volume; (6) the number of grains of benzol per cubic foot of mixture, when:

 - a. The permanent gas is nitrogen and the total pressure is 760 mm of Hg.
 - b. The permanent gas is nitrogen and the total pressure is 700 mm of Hg.
 - c. The permanent gas is carbon dioxide and the total pressure is 700 mm of Hg.
- Arrange the results of these calculations in a table having three columns, a, b, and c, showing the effects of change in total pressure and the nature of the gas on each of the methods of expression of vapor content.
6. Carbon dioxide contains 0.053 pound-mol of water vapor per pound-mol of dry CO₂ at a temperature of 35° C and a total pressure of 750 mm of Hg.
 - a. Calculate the relative saturation of the mixture.
 - b. Calculate the percentage saturation of the mixture.
 - c. Calculate the temperature to which the mixture must be heated in order that the relative saturation shall be 30%.
- Oxygen contains 7.1 grains of water vapor per cubic foot at a temperature of
- a. Calculate the relative saturation of the mixture and its percentage composition by volume if the total pressure is 755 mm of Hg.
 - b. Calculate the percentage saturation of the mixture under the conditions of part a.
 - c. Calculate the weight of water which could be carried by 1 cu ft of the mixture were it saturated at the existing conditions.
8. A mixture of benzol and air at a temperature of 24° C and a pressure of 745 mm of Hg is found to have a dew-point of 11° C.
 - a. Calculate the percentage by volume of benzol.
 - b. Calculate the mols of benzol per mol of air.
 - c. Calculate the weight of benzol per unit weight of air.

9. In the winter an illuminating gas flows from the mains at a temperature of 53°F and a pressure of 758 mm of Hg. The dew-point of the gas is found to be 50°F .

- Calculate the relative humidity of the gas.
- Calculate the molal humidity of the gas.
- Calculate the percentage humidity.
- Calculate the grains of water per cubic foot of wet gas.
- Calculate the relative humidity were the gas warmed to 75°F without changing the pressure.

10. An industrial heating gas is metered at a temperature of 69°F and a pressure of 752 mm of Hg. The relative humidity in the meter is found to be 47%.

The gas has a heating value of 500 Btu per cu ft measured at 60°F under a pressure of 30 in. of Hg and saturated with water vapor. Calculate the heating value per cubic foot measured in the above meter.

11. A flue gas has the following composition as determined by the Orsat apparatus.

CO_2	13.0%
O_2	7.9%
N_2	79.1%

In the stack the gas is at a temperature of 200°C and a pressure of 760 mm of Hg. It is found to have a dew-point of 27°C .

- Calculate the composition by volume of the wet stack gases.
 - Calculate the number of cubic feet of hot, wet flue gas passing up the stack per pound of carbon burned.
 - Calculate the density of the gases in the stack in pounds per cubic foot.
12. The heating value of an illuminating gas is best determined by means of the continuous-flow calorimeter. In such a determination a gas sample is burned which has a volume of 0.2 cu ft. This sample is measured, when saturated with water vapor, at a total pressure of 29.42 in. of Hg and a temperature of 78°F . What volume would be occupied by the same quantity of moisture-free gas as contained in this sample, were it at the gas-testers' standard conditions of 60°F , a pressure of 30.0 in. of Hg, and saturated with water vapor?

13. It is desired to adjust the humidity of the air in a room so that the maximum amount of water vapor shall be present which will not cause condensation if the temperature of the walls should fall to 50°F . If the temperature of the air is 70° and the pressure 750 mm of Hg, calculate the maximum weight of water in grains which may be present, per cubic foot of wet air.

14. It is desired to construct a drier for removing 100 lb of water per hour. Air is supplied to the drying chamber at a temperature of 66°C , a pressure of 760 mm of Hg, and a dew-point of 4.5°C . If the air leaves the drier at a temperature of 35°C , a pressure of 755 mm of Hg, and a dew-point of 24°C , calculate the volume of air, at the initial conditions, which must be supplied per hour.

15. In a process in which benzol is used as a solvent it is desired to evaporate the solvent into a stream of nitrogen in order to avoid fire hazard. The gas enters the evaporator at a temperature of 122°F and a pressure of 745 mm of Hg and leaves at a temperature of 80°F and a pressure of 740 mm of Hg. The gas enters the evaporator containing 0.012 lb of benzol per pound of vapor-free nitrogen and leaves containing 0.161 lb of benzol per pound of nitrogen.

- Calculate the weight of nitrogen which must be supplied for the evaporation of 1 lb of benzol.

- b. Calculate the weight of benzol evaporated per 1000 cu ft of g mixture entering the evaporator.
 - c. Calculate the percentage saturation of the gas mixture leaving the evaporator
16. Air, at a temperature of 60° C, a pressure of 745 mm of Hg, and a percentage humidity of 10%, is supplied to a drier at a rate of 50,000 cu ft per hour. Water is evaporated in the drier at a rate of 60 lb per hour. The air leaves at a temperature of 35° C, and a pressure of 742 mm of Hg.
- a. Calculate the percentage humidity of the air leaving the drier.
 - b. Calculate the volume of wet air leaving the drier per hour.
17. For the best hygienic conditions, air in a living room should be at a temperature of 70° F and a relative humidity of 62%. It is also desirable that fresh air be admitted at such a rate that the air is completely renewed twice each hour. This requires that air be introduced at a volume rate, measured at the conditions of the room, equal to twice the volume of the room.
- a. Calculate the dew-point of the air in the room.
 - b. If air is taken in from the outside at a temperature of 10° F and saturated, calculate the weight of water which must be evaporated, per hour, in order to maintain the above specified conditions in a room having a volume of 3000 cu ft. (Vapor pressure of water at 10° F, over ice = 1.6 mm of Hg; barometric pressure = 743 mm of Hg.)
18. Illuminating gas at a temperature of 90° F and a pressure of 760 mm of Hg enters a gas holder carrying 14 grains of water vapor per cubic foot. If, in the holder, the gas is cooled to 35° F, calculate the weight of water condensed per 1000 cu ft of gas entering the holder. The pressure in the holder remains constant.
19. A gas mixture at a temperature of 27° C and a pressure of 750 mm of Hg contains carbon disulphide vapor such that the percentage saturation is 70%. Calculate the temperature to which the gas must be cooled, at constant pressure, in order to condense 40% of the CS₂ present.
20. A compressed-air tank having a volume of 15 cu ft is filled with air at a gauge pressure of 150 lb per sq in. and a temperature of 85° F and saturated with water vapor. The tank is filled by compressing atmospheric air at a pressure of 14.5 lb per sq in., a temperature of 75° F, and a percentage humidity of 60%. Calculate the amount of water vapor condensed in compressing enough air to fill the tank, assuming that it originally contained air at atmospheric conditions.
21. Air at a temperature of 30° C and a pressure of 750 mm of Hg has a percentage humidity of 60. Calculate the pressure to which this air must be compressed, at constant temperature, in order to remove 90% of the water present.
22. In a process in which benzene is used as a solvent it is evaporated into dry nitrogen. The resulting mixture at a temperature of 24° C and a pressure of 14.7 lb per sq in. has a percentage saturation of 60. It is desired to condense 80% of the benzene present by a cooling and compressing process. If the temperature is reduced to 10° C to what pressure must the gas be compressed?
- The Humidity Charts, Figs. 9 and 10, are to be used in the solution of the following problems and the pressure is assumed to be 1.0 atmosphere.*
23. Air at atmospheric pressure has a wet-bulb temperature of 62° F and a dry-bulb temperature of 78° F.
- a. Estimate the percentage saturation, molal humidity, and the dew-point.
 - b. Calculate the weight of water contained in 100 cu ft of the air.

24. Hydrogen is saturated with water vapor at atmospheric pressure and a temperature of 90° F. The wet gas is passed through a cooler in which its temperature is reduced to 45° F and a part of the water vapor condensed. The gas after leaving the cooler is heated to a temperature of 70° F.

- Estimate the weight of water condensed in the cooler per pound of moisture-free hydrogen.
- Estimate the percentage humidity, wet-bulb temperature, and molal humidity of the gas in its final conditions.

25. It is desired to maintain the air entering a building at a constant temperature of 75° F and a percentage humidity of 40%. This is accomplished by passing the air through a series of water sprays in which it is cooled and saturated with water. The air leaving the spray chamber is then heated to 75° F.

- Assume that the water and air leave the spray chamber at the same temperature. What is the temperature of the water leaving?
- Estimate the water content of the air in the building in pounds of water per pound of dry air.
- If the air entering the spray chamber has a temperature of 90° F and a percentage humidity of 65%, how much water will be evaporated or condensed in the spray chamber per pound of moisture-free air?

26. In a direct-fired evaporator the hot combustion gases are passed over the surface of the evaporating liquid. The gases leaving the evaporator have a dry-bulb temperature of 190° F and a wet-bulb temperature of 145° F. The dry combustion gases contain 11% CO₂. Estimate the percentage saturation of the gases leaving the evaporator, their molal humidity, and their dew-point.

27. At the top of a chimney the flue gas from a gas-fired furnace has a temperature of 180° F and a wet-bulb temperature of 133° F. The composition of the moisture-free flue gas is as follows:

CO ₂	14.1%
O ₂	6.0%
N ₂	79.9%
	<hr/>
	100.0%

- If the temperature of the gases in the stack were reduced to 90° F, calculate the weight of water in pounds which would be condensed per pound-mol of dry gas.
- The gas burned in the furnace is estimated to contain 7% CH₄, 27% CO, and 3% CO₂ by volume; it does not contain any carbon compounds other than these. The gas is burned at a rate of 4000 cu ft per 24 hours measured at a temperature of 65° F, saturated with water vapor. Estimate the weight of water condensed in the chimney per day under the conditions of part a.

28. Air enters a drier at a temperature of 240° F with a dew-point of 55° F. The drier may be assumed to approach adiabatic vaporization in its operation, all the heat being supplied by the air. If the air leaves the drier saturated with water vapor, how much water can be evaporated per 1000 cu ft of entering wet air?

29. A drier for the drying of textiles may be assumed to operate adiabatically. The air enters the drier at a temperature of 160° F with a dew-point of 68° F. It is found that 0.82 lb of water is evaporated per 1000 cu ft of wet air entering the drier. Estimate the percentage saturation and temperature of the air leaving the drier.

30. The boiling-point of benzene (C₆H₆) is 80° C, and its liquid density at the boiling-point is 0.80 gram per cc. Estimate the critical temperature from Equation (5).

CHAPTER V

THERMOPHYSICS

HEAT, ENERGY, AND WORK

The properties of matter which determine the changes in temperature or state of aggregation when heat is removed from or added to a body are known as its thermal properties. The thermal properties which are related to the capacity of a body for absorbing heat under various circumstances are known as *heat capacities* or *specific heats*. Heat which is absorbed with a corresponding change in temperature is termed *sensible heat*. The heat effect involved in a change of state of aggregation without a change of temperature is termed *heat of fusion*, *heat of vaporization*, or *heat of transition*, depending upon the change effected. Heat which is absorbed in this manner without a resultant change in temperature is termed *latent heat*.

The storage of heat as chemical energy and its liberation will be discussed in the next chapter. It is beyond the scope of this book to discuss the transmission of heat and its conversion into mechanical energy.

Internal Energy. The *internal energy* of matter is defined as the total quantity of energy which it possesses as a result of the movements and relative positions of its component molecules and of their component submolecular parts. A part of this energy is present in the form of translational or rotational kinetic energy resulting from the translation or rotation of the individual molecules as units. In a complex molecule a part of it is in the form of energy contained within the molecular unit in the form of kinetic energy resulting from the vibration of its component atomic and subatomic units, and in the form of potential energy resulting from the attractive forces among these submolecular units. These portions of the total internal energy are determined entirely by the temperature at which the matter exists and by its molecular structure. The remainder of the internal energy is in the form of potential energy resulting from the attractive forces among the molecules. This portion of the internal energy is largely determined by the proximity of the molecules to one another as well as by the temperature. The absorption of heat results in a change in quantity of this last form of internal energy. For example, when heat is added to a substance to vaporize it, this heat

is converted into potential energy associated with the greater separation of the molecules in opposition to their mutual attractions.

Equivalent Heat. The total internal energy of a system is increased by the addition of energy in any form. Energy may be added as heat, electrical energy, radiation, or through performing mechanical work on the system in compressing it. It is also possible to increase the internal energy of certain systems by means of external electromagnetic or electrostatic forces, depending on the magnetic and dielectric properties of the system. However, it will be assumed in the following discussion that such effects are absent and that energy is added to a system only as heat, electrical energy, radiation, and work of compression. Thus,

$$\Delta E = q - w_f - w_e \quad (1)$$

where

ΔE = increase in total internal energy

q = heat absorbed

w_f = work in electrical and radiant forms performed by the system

w_e = work of expansion done by the system

It is frequently convenient to consider that the addition of radiant or electrical energy to a system is equivalent to the addition of heat. The *equivalent heat* added to a system will be defined as the total energy added in the forms of heat, radiant, and electrical energies. Thus,

$$h = q - w_e = \Delta E + w_e \quad (2)$$

where

h = equivalent heat added to the system

In dealing with a physical change, in which there is no change in chemical combination, there ordinarily will be no absorption of electrical energy or light, as such, and Equation (2) may be simplified to apply to this particular case.

$$h = q = \Delta E + w_e \quad (3)$$

In its most general sense, the equivalent heat added to a system is equal to the total energy which is added in all forms other than work of compression done on the system.

ENTHALPY OR HEAT CONTENT

An important property of a substance or system which combines internal energy with the work term, pV , is termed *enthalpy* or *heat content* and is defined as

$$H = E + pV \quad (4)$$

where

H = total enthalpy or heat content

E = total internal energy

p = pressure

V = volume

Although absolute values of enthalpy and internal energy content are unknown, changes therein are readily measured. For a finite change in enthalpy Equation (4) becomes

$$\Delta H = \Delta E + \Delta(pV) \quad (5)$$

where ΔH , ΔE , $\Delta(pV)$ = finite related changes in H , E , and pV , respectively.

If a system changes volume under a constant pressure

$$\Delta(pV) = p\Delta V = w_e \quad (6)$$

Combining (6), (5), and (2)

$$\Delta H_p = \quad (7)$$

Thus, whenever heat is added to a system under constant pressure the change in enthalpy is numerically equal to the heat added. Because of this relation enthalpy has been misnamed heat content or total heat. Since the term heat content has become so thoroughly entrenched in the literature it will be retained in this text and used interchangeably with the term enthalpy.

Since total values of enthalpy are unknown it is customary to express values of enthalpy relative to some arbitrarily selected reference state. The temperature, state of aggregation, and pressure of the reference state must be definitely specified. The values of enthalpy so reported are in reality relative enthalpies or values relative to the standard state. The reference state for a gas is usually taken as 0° C and one atmosphere pressure, and for steam as liquid water at 0° C under its own vapor pressure at 0° C. For example, the enthalpy of steam at 200° C and 10 pounds per square inch represents the increase in enthalpy when liquid water at 0° C and its own vapor pressure is vaporized and heated to a temperature of 200° C while its pressure is increased to 10 pounds per square inch.

Heat Units. Since heat is a form of energy it must be expressed in terms of energy units. The fundamental unit of energy in the cgs system is the *erg*, which is the amount of work done by a force of one dyne acting through a distance of one centimeter. Since this unit is inconveniently small for consideration in industrial processes, the *joule*, equal to 10⁷ ergs, is more widely used.

In problems dealing with the production, generation, and transfer of heat it is customary to use special units of energy called heat units. These units are expressed in various terms depending upon which temperature scale and system of weights are employed. The smallest heat unit is the *calorie*, which is the amount of heat required to increase the temperature of one gram of water from 15° to 16° C. One calorie is equivalent to 4.185×10^7 ergs. It will be seen that the calorie is purely an arbitrary unit expressed in terms of the thermal capacity of water and is not based upon the cgs system of measurement. Originally the calorie was defined as the amount of heat required to increase the temperature of water by one degree Centigrade without specifying the temperature range, but it was later found that the heat capacity of water changes slightly with temperature so that it became necessary to specify a definite temperature range. The temperature range from 15° to 16° C was arbitrarily selected since this range corresponds to average room temperatures at which experimental determinations are often conducted. Incidentally, the heat capacity of water is near its minimum and most constant value at ordinary room temperatures. A calorie has also been defined as one-hundredth of the amount of heat required to increase the temperature of one gram of water from 0° to 100° C. This latter unit, called the mean calorie, is no longer in use. The mean calorie is 0.017 per cent larger than the 15° calorie.

In industrial calculations it is always convenient to use heat units larger than the calorie, such as the *kilogram calorie*, *British thermal unit*, or *Centigrade heat unit*. The kilogram calorie, also designated as *Calorie*, is equal to 1000 calories, or it is the amount of heat absorbed in increasing the temperature of one kilogram of water from 15° to 16° C. When measurements are made in English units, employing pounds and the Fahrenheit temperature scale, the British thermal unit or Btu is used. This unit is the quantity of heat absorbed in increasing the temperature of one pound of water from 60° to 61° F. Industries of the United States have often been willing to adopt the Centigrade temperature scale but have refused to abandon the English system of weights. This condition has given rise to a hybrid heat unit known as the Centigrade heat unit, or Chu, which is the amount of heat absorbed in increasing the temperature of one pound of water from 15° to 16° C. The numerical values of heats of formation and reaction, as explained later, are the same when expressed in either Calories per kilogram or Centigrade heat units per pound. For these reasons the Centigrade heat unit has received some favorable acceptance. In the Appendix are factors for the conversion from one system of units to another.

HEAT CAPACITY OF GASES

In a restricted sense *heat capacity* is defined as the amount of heat required to increase the temperature of a body by one degree. *Specific heat* is the ratio of the heat capacity of a body to the heat capacity of an equal weight of water. Specific heat is a property, characteristic of a substance and independent of any system of units, but dependent on the temperatures of both the substance and the reference water. Water at 15° C is usually chosen as the reference.

The unit of heat capacity represents a quantity of heat and may be stated independently of any reference material. The most convenient unit of quantity in dealing with a gas is the mol, since many molal properties of different gases are similar or related. This is particularly true of the molal heat capacities of gases. For this reason the molal heat capacity is a unit which is preferable to either specific heat or heat capacity per unit weight, particularly when applied to gases.

The heat capacity of any quantity of a substance is defined as the heat absorbed per degree temperature rise. Mathematically,

$$C = \frac{dQ}{dT} \quad (8)$$

where

$$\begin{aligned} C &= \text{heat capacity} \\ dQ &= \text{heat added to produce a temperature change, } dT \end{aligned}$$

If a system is heated in such a manner that its total volume remains constant, $dQ = dE - 0$, from Equation (3). The heat capacity under these conditions of constant volume is expressed by

$$C_v = \left(\frac{dE}{dT} \right) \quad (9)$$

Thus, the heat capacity at constant volume, C_v , is equal to the change of internal energy with temperature.

If a system is heated in such a manner that the total pressure remains constant and the volume is permitted to change, heat will be absorbed both to increase the internal energy and to supply the heat equivalent of the external work which is done by the system in expanding. Thus, Equation (8) becomes

$$C_p = \left(\frac{dE}{dT} + \frac{dW}{dT} \right) \quad (10)$$

where C_p is the heat capacity under constant pressure. In the case of a perfect gas,

$$\left(\frac{dV}{dT} \right) = nR$$

Then, the heat capacity at constant pressure, c_p , of one mol of perfect gas is represented by

$$c_p = \left(\frac{dE}{dT} \right) + R = c_v + R \quad (12)$$

$$\text{or} \quad c_p = R \quad (13)$$

where c_p and c_v are the molal heat capacities at constant pressure and volume respectively.

The heat capacity of a substance which expands with rise in temperature is always greater when heated under a constant pressure than when heated under constant volume by the heat equivalent of the external work done in expansion. In the case of a perfect gas the molal heat capacities under the two different conditions differ by the magnitude of the gas law constant, R . The numerical value of R is 1.99 calories per gram-mol per degree Kelvin, or 1.99 Btu per pound-mol per degree Rankine.

In the case of a perfect monatomic gas, such as helium, at a low pressure, it may be assumed that, as a result of the simple molecular structure, the only form of internal energy is the translational kinetic energy of the molecules. The translational kinetic energy per mol of gas may be obtained from Equation (5), Chapter III, page 39, and is equal to the internal energy E in this particular case. Thus,

$$E = \frac{1}{2} mnv^2 = \frac{3}{2} RT \quad (14)$$

Then from Equation (9), for a monatomic gas,

$$c_v = \frac{3}{2} \quad (15)$$

Since R is approximately 2.0 calories per gram-mol per degree Kelvin, the molal heat capacity of a monatomic gas at constant volume is equal to 3.0 calories per gram-mol per degree Kelvin. The molal heat capacity at constant pressure, from Equation (12), will be $3.0 + 2.0$ or 5.0 calories. For monatomic gases the ratio of heat capacities, γ , at 18° C

$$\gamma = \frac{c_p}{c_v} = \frac{5}{3} = \quad (16)$$

For all gases, other than monatomic gases, the molal heat capacity at constant volume is greater than 3.0. In the case of a multatomic gas an increase in heat content is used not only in imparting additional translational kinetic energy, as evidenced by an increase in temperature and an increasing velocity of translation, but also to impart increased energies of rotation and vibration of the molecular and submolecular units.

In general, gases of similar molecular complexity have nearly identical molal heat capacities. For example, the diatomic gases such as oxygen, nitrogen, hydrogen, and carbon monoxide all have practically equal molal heat capacities. The halogens have slightly higher heat capacities. As the molecular complexity increases, the molal heat capacity also increases. For example, water vapor and hydrogen sulphide have heat capacities higher than those of oxygen and nitrogen; carbon dioxide, sulphur dioxide, and nitrous oxide have heat capacities similar to but somewhat greater than that of water in the vapor state. The hydrocarbon gases have still higher molal heat capacities which increase with increase in the molecular weight of the gas.

The usual empirical form of the molal heat capacity equations is,

$$c_p = a + bt + ct^2 \quad (17)$$

where t is temperature and a , b , and c are experimentally determined constants. The empirical equations of E. D. Eastman¹ for the effects of temperature on molal heat capacities of gases at ordinary atmospheric pressures have been selected as the most acceptable and are presented in Tables I and II. These equations have been based upon the most reliable of experimental data, although they are not in exact agreement with the values given in the International Critical Tables, 1929. The latter values are particularly low for carbon dioxide and water vapor. The temperature range over which each equation is valid and the probable accuracy are also indicated. Only heat capacities at constant pressure are presented. Heat capacities at constant volume may be obtained by means of Equation (13).

Data for hydrocarbon gases are presented in Chapter VII, page 219.

The experimental determinations of heat capacities from calorimetric measurements are extremely difficult to make with any high degree of precision. Recently theoretical values of heat capacities over a wide temperature range have been calculated from quantum mechanics, using the Planck-Einstein equation. The theoretical equations have been reduced to simple empirical form by Bryant² with results which agree within 3 per cent with the best data obtained by direct experiment. It is likely that in the future all data on heat capacities will be calculated by this method especially for gases of high molecular weight.

¹ E. D. Eastman, "Specific Heat of Gases," Bureau of Mines Technical Paper 445 (1929).

² W. M. D. Bryant, *Ind. and Eng. Chem.* **25**, 820 (1933).

TABLE I

Molal Heat Capacities of Gases at Constant Pressure of 1 Atmosphere
Metric Units

c_p = Calories per kilogram-mol per degree Centigrade.

t = temperature in degrees Centigrade.

T = temperature in degrees Kelvin.

N_2 , O_2 , CO , NO , HCl , HI , HBr , F_2

$$c_p = 6.935 + 0.000677t + 0.13 \times 10^{-6}t^2 \quad (1.5\% \text{ error from } 0^\circ \text{ to } 2200^\circ \text{ C})$$

$$= 6.761 + 0.000606T + 0.13 \times 10^{-6}T^2$$

H_2 , HF

$$c_p = 6.943 + 0.00040t + 0.22 \times 10^{-6}t^2 \quad (1.5\% \text{ error from } 0^\circ \text{ to } 2200^\circ \text{ C})$$

$$= 6.850 + 0.00028T + 0.22 \times 10^{-6}T^2$$

H_2O

$$c_p = 8.361 + 0.000883t + 0.13 \times 10^{-6}t^2 \quad (1.5\% \text{ error from } 0^\circ \text{ to } 2200^\circ \text{ C})$$

$$= 8.217 + 0.000173T + 0.13 \times 10^{-6}T^2$$

NH_3

$$c_p = 8.42 + 0.0063t \quad (1.5\% \text{ error from } 0^\circ \text{ to } 500^\circ \text{ C})$$

$$= 6.70 + 0.0063T$$

H_2S

$$c_p = 8.183 + 0.0036t \quad (5 \text{ to } 10\% \text{ error from } 0^\circ \text{ to } 300^\circ \text{ C})$$

$$= 7.199 + 0.0036T$$

Cl_2 , S_2

$$c_p = 8.66 + 0.0003t \quad (5\% \text{ error from } 0^\circ \text{ to } 2200^\circ \text{ C})$$

$$= 8.58 + 0.0003T$$

CO_2 , SO_2

$$c_p = 9.085 + 0.0048t - 0.83 \times 10^{-6}t^2 \quad (2.5\% \text{ error from } 0^\circ \text{ to } 2200^\circ \text{ C})$$

$$= 7.713 + 0.0053T - 0.83 \times 10^{-6}T^2$$

Monatomic Gases (He , A , etc., and the metallic vapors)

$$c_p = 4.98$$

CH_4

$$c_p = 8.52 + 0.0096t \quad (5.0\% \text{ error from } -100^\circ \text{ to } 150^\circ \text{ C})$$

$$= 5.90 + 0.0096T$$

These equations are expressed in graphical form in Fig. 11.

Effect of Pressure on the Heat Capacity of Gases. The heat capacities of gases are not greatly affected by small variations in pressure at low pressures. However, at low temperatures, near the normal boiling-points, the effect of pressure is very marked, heat capacities increasing very rapidly with increase in pressure and becoming infinite at the critical point. The effects of high pressures on heat capacities are discussed in detail in Chapter XIII. As the temperature is increased, the effect of pressure upon heat capacity gradually diminishes.

TABLE II

Molal Heat Capacities of Gases at Constant Pressure of 1 Atmosphere
English Units

c_p = Btu per pound-mol per degree Fahrenheit.
 t_f = temperature in degrees Fahrenheit.

$N_2, O_2, CO, NO, HCl, HI, HBr, F_2$

$$c_p = 6.923 + 0.000373t_f + 0.40 \times 10^{-7}t_f^2$$

H_2, HF

$$c_p = 6.937 + 0.000218t_f + 0.68 \times 10^{-7}t_f^2$$

H_2O

$$c_p = 8.346 + 0.000465t_f + 0.414 \times$$

$$c_p = 8.308 + 0.0035t_f$$

$$c_p = 8.119 + 0.002t_f$$

Cl_2, S_2

$$c_p = 8.657 + 0.000167t_f$$

CO_2, SO_2

$$c_p = 9.000 + 0.0027t_f - 0.256 \times$$

Monatomic Gases (He, Ar, etc., and the metallic vapors)

$$c_p = 4.98$$

CH_4

$$c_p = 8.33 + 0.0053t_f$$

These equations are expressed in graphical form in Fig. 13.

Heat Capacity of Gases Based on Various Weight and Volume Units. The advantages of the use of molal quantities have been repeatedly stressed. Nevertheless, many industrial engineers do not employ these units. Industrial gases are usually measured by volume, in cubic feet or cubic meters, and solids by weight, in pounds. From the equations given above for the molal heat capacities of gases, values may be readily calculated for any other units of weight or volume, such as Calories per kilogram, Calories per cubic meter, Btu per pound, and Btu per cubic foot.

Whenever heat capacities are based on unit volumes, the basic quantity of gas involved is that contained in a unit volume measured at standard conditions of temperature and pressure and not at the existing conditions. The heat capacity per unit volume refers to the heat capacity of a very definite and constant weight of gas, regardless of the temperature and pressure. For example, the heat capacity per cubic meter of oxygen at 1000° C signifies the heat capacity at 1000° C of the weight of gas contained in 1 cubic meter at standard conditions, or of 1.44 kilograms of oxygen. It does not signify the heat capacity of the oxygen contained in 1 cubic meter at the given temperature and pres-

sure. This distinction must always be kept in mind in speaking of the heat capacities of unit volumes of gases at various temperatures.

In the fuel gas industries an unusual unit of gas quantity is employed as the standard. This unit is the quantity of gas contained in 1000 cubic feet, measured at a pressure of 30 inches of mercury, a temperature of 60° F and saturated with water vapor. This volume of gas corresponds to 2.597 pound-mols of dry gas containing 0.046 pound-mol of water vapor, or 2.643 pound-mols of the mixture. The heat capacity of the weight of gas equivalent to 1000 cubic feet as measured in the gas industry at 30 inches of mercury, saturated, and at 60° F can be obtained by multiplying the molal heat capacity of that gas, expressed in Btu per pound-mol per degree Fahrenheit, by the factor 2.643.

Mean Heat Capacities of Gases. The heat capacity equations given in Tables I and II represent the values of heat capacities at any temperature, t . In heating a gas from one temperature to another it is desirable to know the mean or average heat capacity over that temperature range. The total heat required in heating the gas can then be readily calculated by simply multiplying the number of mols of gas by the mean molal heat capacity and by the temperature rise. This method is simpler than employing direct integration of the heat capacity formulas for each problem. For gases of the air group where the temperature coefficient is nearly constant, and over short temperature ranges for other gases, accurate results may be obtained by simply employing the heat capacity at the average temperature as the mean heat capacity. Even for a gas such as carbon dioxide, whose temperature coefficient of heat capacity changes markedly with temperature, the heat capacity at 500° C is only 0.6 per cent higher than the correct mean value over the temperature range from 0° to 1000° C.

The mean heat capacity over any given temperature range may be calculated by integrating the general equation for instantaneous values over the desired temperature range as follows:

$$\begin{aligned}\text{Mean } c_p &= \frac{\int_{t_1}^{t_2} c_p dt}{t_2 - t_1} = \\ &= a + \frac{b}{2}(t_2 + t_1) + \frac{c}{3}(t_2^2 + t_2 t_1 + t_1^2)\end{aligned}\quad (18)$$

where t_2 is the higher and t_1 the lower temperature. For mean molal heat capacities between 0° and t ° this equation simplifies to:

$$\text{Mean } c_p \text{ (from 0 to } t) = a + \frac{bt}{2} + \frac{ct^2}{3}\quad (19)$$

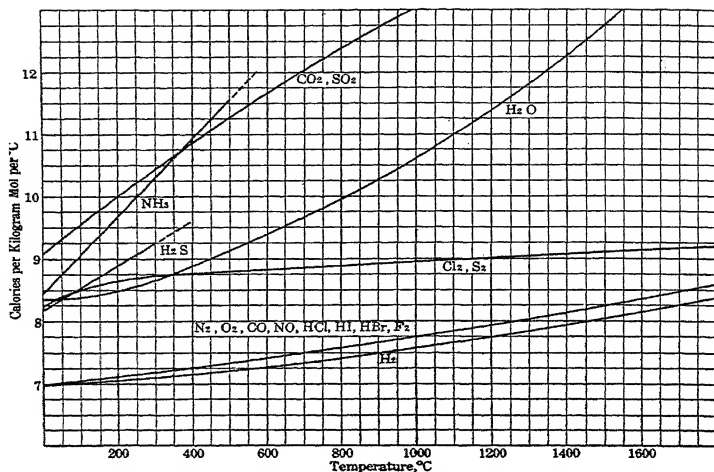
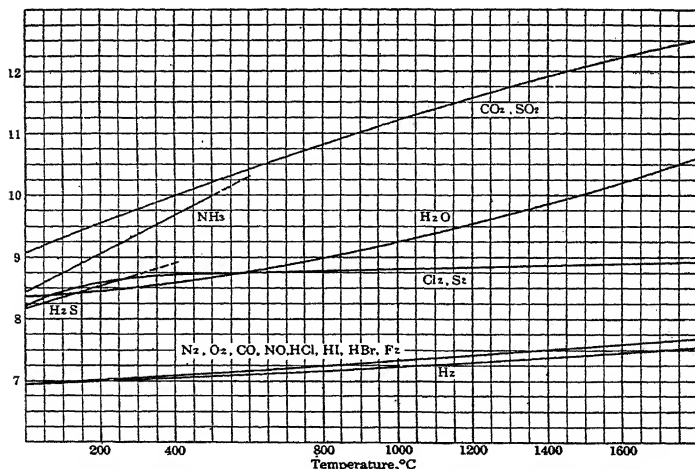


FIG. 11. Molal Heat Capacities of Gases at Constant Pressure.
Metric Units.



12. Mean Molal Heat Capacities of Gases at Constant Pressure.
Metric Units. (From 0° to t ° C.)

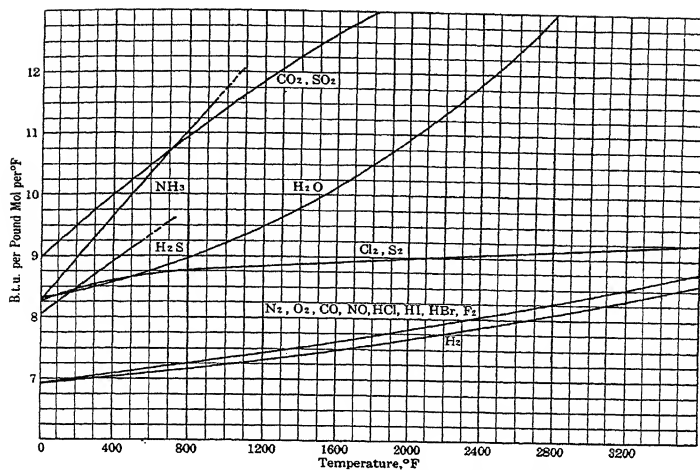


FIG. 13. Molal Heat Capacities of Gases at Constant Pressure.
English Units.

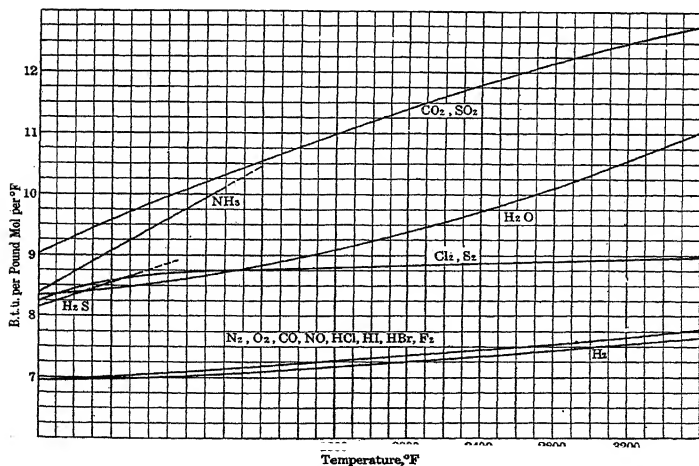


FIG. 14. Mean Molal Heat Capacities of Gases at Constant Pressure.
English Units. (From 32° to t ° F.)

TABLE III
 HEAT CAPACITIES OF LIQUIDS

Data from International Critical Tables unless otherwise indicated.

 c_p = heat capacity, calories per gram per °C at t° C.

 a = temperature coefficient in equation: $c_p \approx c_{p0} + at$,
 applying over the indicated temperature range.

Liquid	Formula	t° C	c_p	Temp. Range		
Mercury.	Hg	0	.0335			
		60	.0330			
		100	.0329			
		200	.0329			
		280	.0332			
Water.	H ₂ O	0	.008			
		15	.001			
		100	.002			
		200	.016			
		300	.039			
Sulphur dioxide	SO ₂	-20	.3130			
Sulphuric acid.	H ₂ SO ₄			.327	.00028	11° to 140°
Ammonia.....				.339	.00038	10° to 45°
		-40	1.051			
		0	1.098			
		60	1.215			
		100	1.479			
Silicon tetrachloride	SiCl ₄	2 to 50	0.200			
Sodium nitrate.....	NaNO ₃	350	0.4030			
Carbon tetrachloride	CCl ₄	20	0.201	0.198	.000031	0° to 70°
Carbon disulphide...	CS ₂			0.235	.000246	100° to +150°
Chloroform.....	CHCl ₃	15	0.226	0.221	.000330	-30° to +60°
Formic acid.....	CH ₂ O ₂	0	0.496		.000709	40° to 140°
Methyl alcohol.....	CH ₄ O	0	0.566			
		40	0.616			
Acetic acid.....	C ₂ H ₄ O ₂			0.468	0.000929	0° to 1
Ethyl alcohol.....	C ₂ H ₆ O	-50	0.473			
		0	0.535			
		25	0.580			
		50	0.652			
		100	0.824			
		150	1.053			
Glycol.....	C ₂ H ₆ O ₂	0	0.544	0.544	0.00119	-20° to +200°
Allyl alcohol.....	C ₃ H ₆ O	0	0.3860			
		21 to 96	0.665			
Acetone.....	C ₃ H ₆ O			0.506	0.000764	-30° to +60°
Propane.....	C ₃ H ₈	0	0.576	0.576	0.001502	-30° to +20°
Propyl alcohol.....	C ₃ H ₈ O	-50	0.456			
		0	0.480			
		+50	0.654			
Glycerol.....	C ₃ H ₈ O ₃	-50	0.485			
		0	0.540			
		+50	0.598			
		+100	0.668			
Ethyl acetate.....		20	0.478			
n-butane.....	C ₄ H ₁₀	0	0.550	0.550	0.00191	-15° to +20°
Ether.....	C ₄ H ₁₀ O	0	0.529			
		30	0.548			
		120	0.802			

TABLE III. (Continued)

Liquid	Formula	c_p		Temp. Range		
Isopentane...	C_5H_{12}	0	0.512			
		8	0.526			
		10	0.358			
		50	0.329			
Nitrobenzene.	$C_6H_5NO_2$	120	0.393			
		5	0.389			
		20	0.406			
		60	0.444			
Benzene.		90	0.473			
		0	0.478			
		50	0.521			
		100	0.547			
<i>n</i> -Hexane.	C_6H_{14}	20 to 100	0.600			
Toluene..	C_7H_8	0	0.386			
		50	0.421			
		100	0.470			
		0 to 50	0.507			
<i>n</i> -Heptane.	C_7H_{16}	30	0.518	0.476	0.00142	30° to 80°
Decane (B.-P 172°)	$C_{10}H_{22}$	0 to 50	0.502			
<i>n</i> -Hexadecane.....	$C_{16}H_{34}$	0 to 50	0.496			
Stearic acid.....	$C_{18}H_{36}O_2$	75 to 137	0.550			
Diphenyl*.....	$C_{12}H_{10}$			0.7300	0.00120	80° to 300°

* Forrester, Brugmann, and Cummings, Ind. Eng. Chem. **23**, 340 (1931).

Values for mean molal heat capacities are plotted in Figs. 12 and 14 for the temperature range from 0° C to t ° C and from 32° F to t ° F.

The quantity of heat absorbed in raising the temperature of a unit weight of material from t_1 to t_2 is given by:

$$q = -c_{p_1}t_1 \quad (20)$$

where

t_2 is the upper temperature

t_1 is the lower temperature

c_{p_2} and c_{p_1} are the mean heat capacities over the range from the reference temperature, 0° C, to temperatures t_2 and t_1 respectively

The mean heat capacity over the temperature range from t_1 to t_2 is then:

$$\text{Mean } c_p \text{ (from } t_1 \text{ to } t_2) = \frac{c_{p_2}t_2 - c_{p_1}t_1}{t_2 - t_1} \quad (21)$$

By use of Equation (21) mean heat capacities over any temperature range can be obtained directly from Fig. 12 or 14.

HEAT CAPACITIES OF LIQUIDS AND SOLUTIONS

No generalizations can be stated regarding the heat capacities of liquids except that they usually increase with an increase in temperature. Water has a higher specific heat than any other substance, with the exception of liquid ammonia and a very few organic compounds. The heat capacity of water is at its minimum at 30° C. The specific heats of aqueous solutions in general decrease with increasing concentration of solute. In dilute solutions the heat capacity of aqueous solutions is nearly equal to the heat capacity of the water present. The heat capacities of some common aqueous solutions of acids, bases, and salts are shown graphically in Figs. 15, 16, 17, 18, and 19. The heat capacities of the solutions all correspond to a temperature of about 20° C. In Table III are values of the specific heats of some common liquids. Data for petroleum fractions are presented in Chapter VII, page 218.

Partial Heat Capacities. The heat capacity of any heterogeneous physical mixture is equal to the sum of the heat capacities of the components present. For example, the heat capacity of a mixture of sand and salt is simply equal to the sum of the heat capacities of the two materials. Similarly, in a mixture of gases at a low pressure, the molal heat capacity of the mixed gas is equal to the sum of the products of the molal heat capacities of each component gas multiplied by its respective mol fraction. Thus,

$$c_p = N_A c_{pA} + N_B c_{pB} + N_C c_{pC} + \dots \quad (22)$$

where

c_p = molal heat capacity of mixture.

c_{pA}, c_{pB} = molal heat capacities of components $A, B \dots$

N_A, N_B = mol fractions of components $A, B \dots$

The heat capacity of a liquid solution cannot be determined from the heat capacities of the pure components by any such simple, additive method. Usually neither the solvent nor the solute adds its normal heat capacity to the heat capacity of the solution. The actual heat capacity which is contributed to the total heat capacity of the solution by the presence of each unit weight of one of its components is called the *partial heat capacity* of this component. If C is the total heat capacity of a solution containing w_1 grams of solvent and w_2 grams of solute,

$$C = w_1 c_1 + w_2 c_2 \quad (23)$$

where

$w_1 c_1$ = partial heat capacity of solvent, per gram

$w_2 c_2$ = partial heat capacity of solute, per gram

The term $w_1 c_1$ of Equation (23) represents that part of the total heat capacity of the solution which results from the presence of the w_1 grams of solvent. The partial heat capacity of the solvent, c_1 , depends on the natures of both solvent and solute and upon their relative proportions in the solution. If an infinitesimal amount of solvent, dw_1 , is added to the solution defined by Equation (23), the concentration of

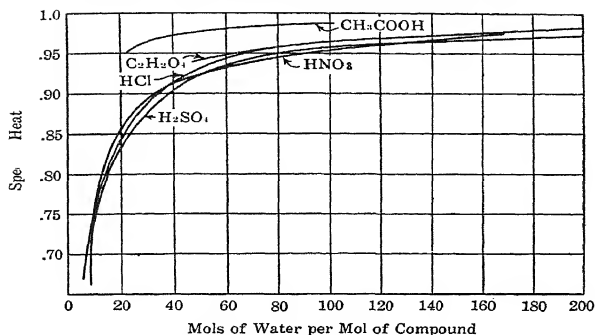


FIG. 15. Specific Heats of Aqueous Solutions of Acids at 20° C.

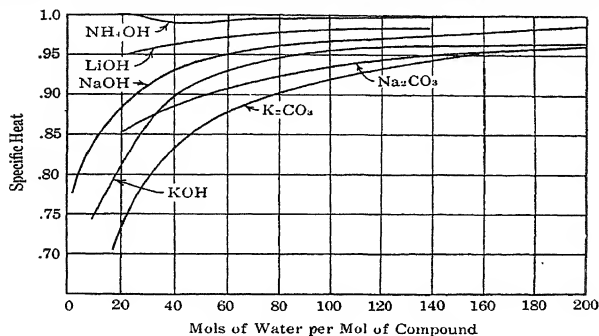


FIG. 16. Specific Heats of Aqueous Solutions of Bases at 20° C.

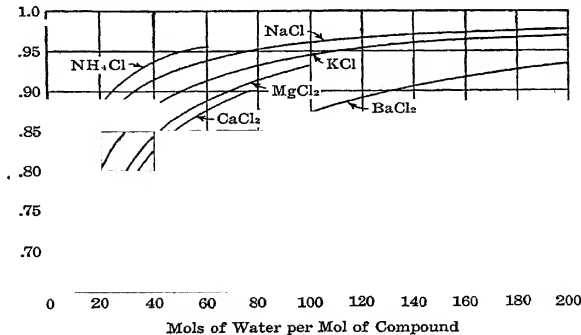


FIG. 17. Specific Heats of Aqueous Solutions of Chlorides at 20° C.

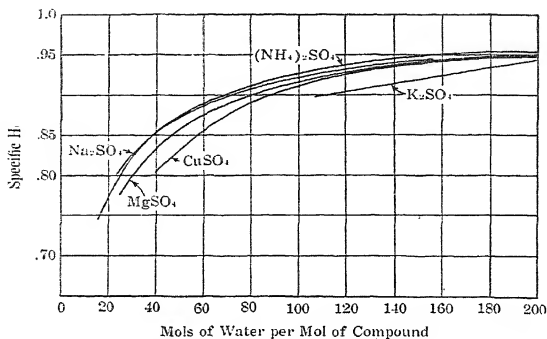


Fig. 18. Specific Heats of Aqueous Solutions of Sulphates at 20° C.

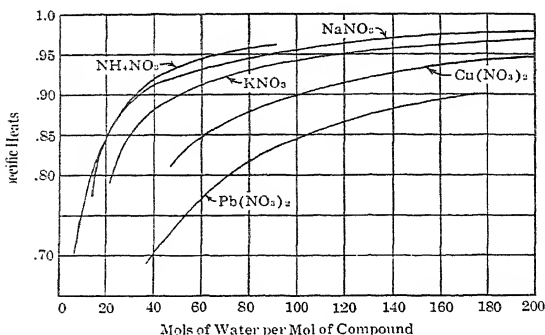


Fig. 19. Specific Heats of Aqueous Solutions of Nitrates at 20° C.

the solution will be practically unchanged but its heat capacity will be increased by an amount dC which will equal $dw_1\bar{c}_1$. Then,

$$\left(\frac{\partial w_1}{\partial w_1}\right)_u \quad (24)$$

Thus, the partial heat capacity of the solvent, \bar{c}_1 , is equal to the increase in the heat capacity of the solution when 1 gram of the solvent is added to so large a quantity of solution that no change in composition results. Similarly,

$$\left(\frac{\partial C}{\partial w_2}\right)_{w_1} = \bar{c}_2 \quad (25)$$

Equation (23) may also be written to represent the heat capacity per unit weight of solution, c .

$$C = \frac{w_1}{w_1 + w_2} \bar{c}_1 + \frac{w_2}{w_1 + w_2} \bar{c}_2$$

or
where

$$c = f_1 \bar{c}_1 + f_2 \bar{c}_2 \quad (26)$$

f_1 = weight fraction of solvent
 f_2 = weight fraction of solute

Exactly the same type of reasoning applies when the quantities and compositions of a solution are expressed in molal units. Thus,

$$c' = N_1 \bar{c}_1' + N_2 \bar{c}_2' \quad (27)$$

where

c' = molal heat capacity of solution
 N_1, N_2 = mol fractions of solvent and solute
 \bar{c}_1', \bar{c}_2' = partial molal heat capacities of solvent and solute, respectively

By comparison of Equations (22) and (27) it is seen that in an ideal mixture of gases the partial molal heat capacity of each component gas, \bar{c}_p , is identical with the molal heat capacity, c_p , of the pure gas. Likewise, in mechanical mixtures, as mixed solids, emulsions, or suspensions, the partial heat capacity of each component is unaltered by change of its proportion in the mixture. In liquid solutions whose total heat capacity per gram of solution is a linear function of concentration, the partial heat capacity of each component is also the same as that of the component in the pure state. However, for most aqueous solutions the partial heat content of either solute or solvent may vary greatly with concentration and may even assume a negative value; that is, the addition of a small amount of one component to a solution may actually lower the total heat capacity of the solution.

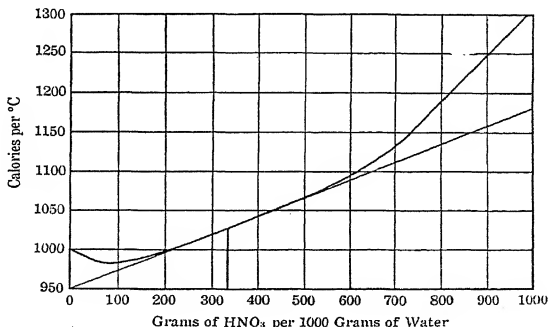


FIG. 20. Total Heat Capacities of Aqueous Solutions of Nitric Acid per 1000 grams of Water.

Lewis and Randall¹ present several methods of calculating partial properties of solutions. Two of these graphical methods will be illustrated by calculating the partial molal heat capacities of aqueous nitric acid. The heat capacities, c , of nitric acid solutions are given in Table IV, expressed in calories per gram of solution per degree Centigrade, for a range of concentrations from 0 to 100 per cent, HNO_3 .

¹"Thermodynamics," p. 36, McGraw-Hill (1923).

Method 1. Tangent Slopes. If the heat capacity data for a solvent-solute system are expressed in terms of the heat capacity of the solution *per unit quantity of solvent*, the partial heat capacity of the solute may be determined from Equation (25). In dealing with aqueous solutions it is convenient to use 1000 grams of water (55.51 gram-mols) as the basic unit quantity of solvent. The number of gram-mols of solute dissolved in this quantity of water is equal to the molality of the solution. Values of total heat capacities on this basis, C , are plotted against concentrations in grams of nitric acid per 1000 grams of water in Fig. 20. From the slope of the tangent to the curve at any point the partial heat capacity of the solute, per gram, can be obtained from Equation (25).

For example, where $w_2 = 333$ the slope of the tangent is $\frac{1182 - 950}{1000} = 0.232$, which is the partial heat capacity, \bar{c}_2 , per gram of HNO_3 in a solution of this particular concentration, 333 grams of HNO_3 per 1000 grams of water.

When \bar{c}_2 is known, the partial heat capacity of the solvent, \bar{c}_1 , may be calculated from Equation (23).

TABLE IV
PARTIAL HEAT CAPACITIES OF HNO_3 AND WATER IN
AQUEOUS SOLUTIONS OF NITRIC ACID

c = heat capacity in calories per gram of solution per degree Centigrade.

\bar{c}_1 = partial heat capacity of water in calories per gram of solution per degree Centigrade.

\bar{c}_2 = partial heat capacity of HNO_3 in calories per gram of solution per degree Centigrade.

Percentage HNO_3	c	\bar{c}_1	\bar{c}_2
0	1.00	1.0	-0.45
1	0.985	1.00	-0.36
2.5	0.965	1.00	-0.26
5	0.935	0.99	-0.18
10	0.888	0.97	0.10
15	0.848	0.97	0.17
20	0.807	0.96	0.20
25	0.770	0.95	0.23
30	0.737	0.94	0.25
40	0.669	0.85	0.40
45	0.662	0.77	0.54
50	0.655	0.76	0.55
60	0.634	0.76	0.55
70	0.610	0.80	0.53
80	0.581	0.87	0.51
90	0.533	1.07	0.47
98	0.475	1.28	0.46
100	0.46	1.42	0.46

For example, from Fig. 20, where $w_2 = 333$, C is equal to 1025. Then,

$$\bar{c}_1 = \frac{C - \bar{c}_2 w_2}{w_1} = \frac{1025 - (0.232 \times 333)}{1000} = 0.949$$

Making calculations on the basis of 1000 grams of water does not prove satisfactory for high concentrations because values of w_2 and C approach infinity. Instead, for concentrations above 50 per cent it is better to reverse the procedure by using as the basis of calculation 1000 grams of nitric acid, or some other convenient weight, for example, 1 mol. The values of \bar{c}_1 and \bar{c}_2 calculated by Method 1 are plotted in curves I and II of Fig. 21 and tabulated in Table IV.

Partial molal heat capacities may be calculated in the same manner by plotting the total heat capacity per 1000 grams of water against the *mols* of solute per 1000 grams of water. The partial molal heat capacity of the solute is represented by the slope of a tangent to this curve. The partial molal heat capacity of the solvent may then be calculated from Equation (27).

Method 2. Tangent Intercepts. The heat capacity per unit weight of solution is plotted against percentage composition by weight as in curve III of Fig. 21. A tangent is drawn to this curve at the desired concentration. The intersection of this tangent with the 0 per cent concentration ordinate gives the partial heat capacity of the solvent, and the intersection with the 100 per cent ordinate gives the partial heat capacity of the solute. For example, at a concentration of 25 per cent HNO_3 , the tangent, AF (Fig. 21), intersects the 0 per cent HNO_3 ordinate at 0.951 and the 100 per cent ordinate at 0.232. These are the values of c_1 and \bar{c}_2 , respectively, expressed in calories per gram per degree Centigrade. A proof of this relationship follows:

Let:

C = total heat capacity of a solution containing w_1
grams of solvent and w_2 grams of solute
 c = heat capacity per gram of solution
 f_1 = weight fraction of solvent
 f_2 = weight fraction of solute

$$\text{Then,} \quad c = \frac{C}{w_1 + w_2} \quad (28)$$

$$(29)$$

Referring to Fig. 21, the slope at any point, E , is equal to $\frac{dc}{df_2}$; also,

$$OA = OB + AB = c - f_2 \frac{dc}{df_2} \quad (30)$$

Variation in the percentage of solute, f_2 , may be produced by addition or removal of only solvent, keeping w_2 constant. Treating w_2 as constant and differentiating Equation (28) with respect to

$$\frac{dc}{dw_1} = \frac{dC}{dw_1} - \frac{dw_1}{(w_1 + w_2)^2} \quad (31)$$

Differentiating (29) with respect to w_1 with w_2 constant,

$$\frac{df_2}{dw_1} = - \quad (32)$$

Combining (31) and (32)

$$\frac{dc}{df_2} = \frac{dC}{dw_1} \quad (33)$$

Substituting (33) in (30)

$$(34)$$

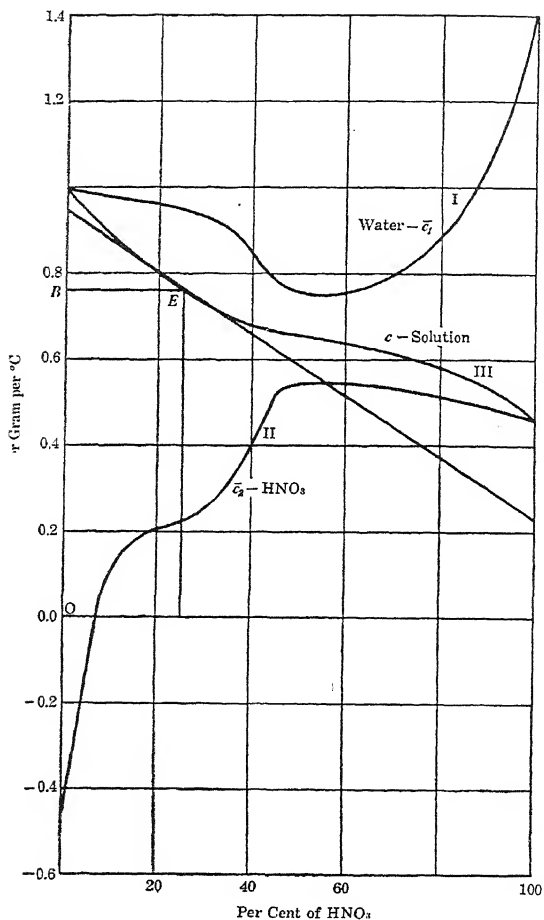


FIG. 21. Partial Heat Capacities of HNO₃ and Water in Aqueous Solutions of Nitric Acid.

Substituting (28) and (29) in (34),

$$OA = c + \frac{dC}{dw} - c = \quad (35)$$

Since w_2 was treated as constant in all differentiations, $\frac{dC}{dw_1} = \left(\frac{\partial C}{\partial w_1}\right)_{w_2}$ and from Equation (24)

$$OA = \bar{c}_1 \quad (36)$$

Similarly, it may be shown that

$$OF = \bar{c}_2 \quad (37)$$

This same method may be used for determining partial molal heat capacities. In this case heat capacities per mol of solution are plotted against mol fractions of solute. The intercepts at 0 per cent and 100 per cent solute are then, respectively, the partial molal heat capacities of the solute and the solvent.

HEAT CAPACITIES OF SOLIDS

According to the law of Petit and Dulong the atomic heat capacities of the crystalline solid elements are constant and equal to 6.2 calories

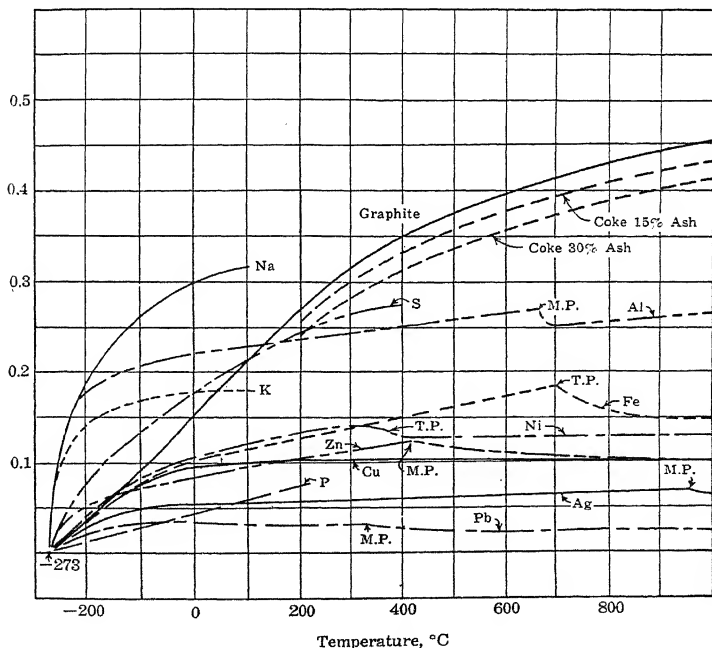


FIG. 22. Instantaneous Specific Heats of Common Elements and Coke.

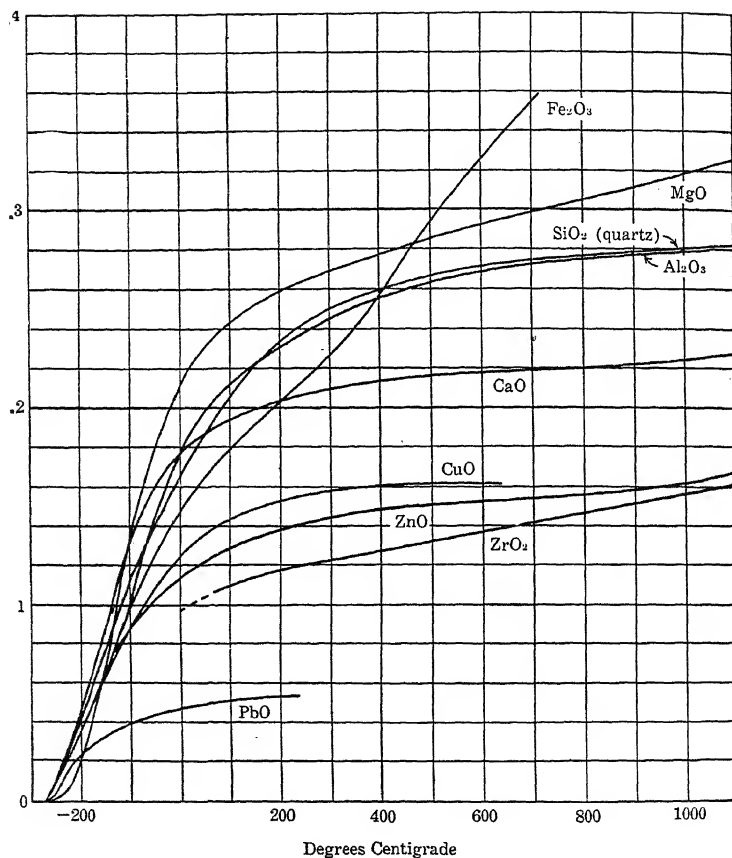


FIG. 23. Instantaneous Specific Heats of Some Common Oxides.

per gram-atom. This rule applies satisfactorily to all elements having atomic weights above 40 when applied to constant volume conditions at room temperatures. From kinetic theory, Boltzmann showed that the atomic heat capacity of the elements at constant volume reaches a maximum value of $3R = 5.97$ calories per degree. The atomic heat capacities of elements such as carbon, hydrogen, boron, silicon, oxygen,

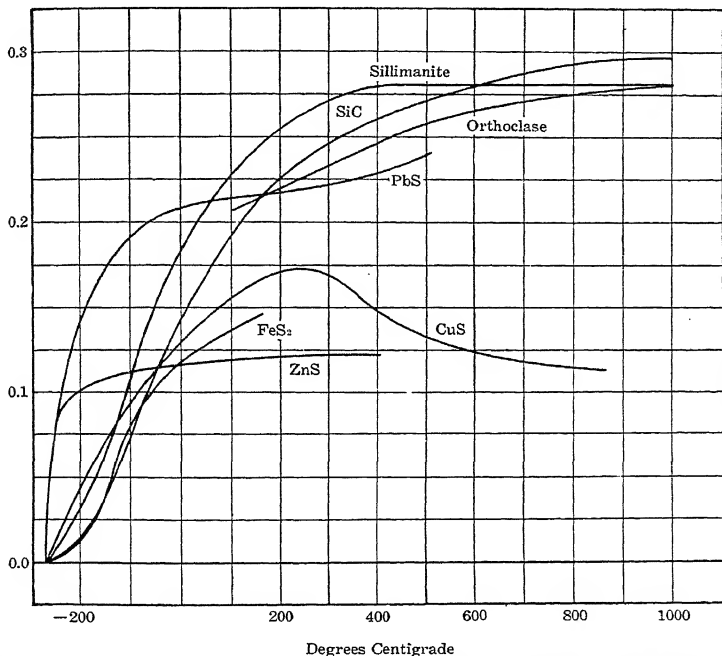


FIG. 24. Instantaneous Specific Heats of Sulphides and Refractory Materials.

fluorine, phosphorus, and sulphur are much lower than the rule indicates. At increasing temperatures, however, the atomic heat capacities of these elements also approach the value 6.2. The atomic heat capacities of all elements decrease greatly with decrease in temperature, approaching a value of zero at absolute zero temperature when in the crystalline state.

Kopp's Rule. The heat capacity of a solid compound is approximately equal to the sum of the heat capacities of the constituent elements. This generalization was first shown by Kopp to be approxi-

mately correct, provided the following atomic heat capacities were assigned to the elements: C, 1.8; H, 2.3; B, 2.7; Si, 3.8; O, 4.0; F, 5.0; P, 5.4; S, 5.4; all others, 6.2. This rule should be used only where experimental values are lacking. Since the heat capacities of solids increase with temperature it is obvious that the above empirical rule is inexact. In general, the heat capacities of compounds are higher in the liquid than in the solid state. At the melting-point the two heat capacities are nearly the same.

The heat capacity of a heterogeneous mixture is a simple additive property, the total heat capacity being equal to the sum of the heat capacities of the component parts. When true solutions are formed, this simple additive property no longer exists, as was pointed out in the preceding section.

The specific heats of various elements and oxides are presented graphically in Figs. 22 and 23. In Fig. 24 are specific heats of a few sulphides and various refractory materials. The heat capacities of many other common solids are tabulated in Table V. It will be noted that no general prediction can be made as to the quantitative effect of temperature on these heat capacities. Transition-points, T-P., indicating changes in crystalline structure, and melting-points, M-P., correspond to abrupt changes in the heat capacity relationships.

TABLE V

HEAT CAPACITIES OF SOLID SUBSTANCES

Data from the International Critical Tables unless otherwise indicated

 C_p = calories per gram per °C or

= Calories per kilogram per °C

Inorganic Compounds

Substance	Formula	$t^{\circ}\text{C}$	C_p
Aluminum sulphate...	$\text{Al}_2(\text{SO}_4)_3$	50	0.184
Aluminum sulphate...	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$	34	0.353
Ammonium chloride...	NH_4Cl	0	0.357
Antimony trisulphide.	Sb_2S_3	0	0.0830
(stibnite).....		100	0.0884
Arsenious oxide.....	As_2O_3	0	0.117
		40	0.122
Barium carbonate.	BaCO_3	0	0.100
		100	0.110
		400	0.123
		800	0.130
Barium chloride....	BaCl_2	0	0.0853
		100	0.0945
Barium sulphate...	BaSO_4	0	0.1112
		1000	0.1448
Cadmium sulphide.	CdS	0	0.0881
		50	0.0902
Cadmium sulphate.	$\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	0	0.1950
Calcium carbonate.	CaCO_3	0	0.182
		200	0.230
		400	0.270
Calcium chloride...	CaCl_2	61	0.164
Calcium chloride...	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	0	0.321
Calcium fluoride...	CaF_2	0	0.204
		40	0.212
		80	0.216
Calcium sulphate.	CaSO_4	0	0.1691
		400	0.2275
Calcium sulphate.	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0	0.2650
		50	0.198
Chromium oxide...	Cr_2O_3	0	0.168
		50	0.188
Copper sulphate...	CuSO_4	0	0.148
Copper sulphate...	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	0	0.1717
Copper sulphate...	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$	9	0.2280
Copper sulphate...	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0	0.2560
Ferrous carbonate.	FeCO_3	54	0.193
Ferrous sulphate...	FeSO_4	45	0.167
Lead carbonate....	PbCO_3	32	0.080
Lead chloride.....	PbCl_2	0	0.0649
		200	0.0704
		400	0.0800
Lead nitrate.....	$\text{Pb}(\text{NO}_3)_2$	45	0.1150
Lead sulphate.....	PbSO_4	45	0.0838
Magnesium chloride.	MgCl_2	48	0.193
Magnesium sulphate.	MgSO_4	61	0.222
Magnesium sulphate.	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	9	0.239
Magnesium sulphate.	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	9	0.349
Magnesium sulphate.	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	12	0.361

TABLE V. (Continued)

Substance	Formula	$t^{\circ}\text{C}$	C_p
Manganese dioxide.	MnO_2	0	0.152
Manganic oxide. . . .	Mn_2O_3	58	0.162
Manganous oxide. . .	MnO	58	0.158
Mercuric chloride. .	HgCl_2	0	0.0640
Mercuric sulphide. .	HgS	0	0.0506
Mercurous chloride	Hg_2Cl_2	0	0.0499
Nickel sulphide. . . .	NiS	0	0.116
		100	0.128
		200	0.138
Potassium chlorate. .	KClO_3	0	0.1910
Potassium chloride. .	KCl	200	0.2960
		0	0.1625
		200	0.1725
		400	0.1790
Potassium chromate. .	K_2CrO_4	46	0.1864
Potassium dichromate.	$\text{K}_2\text{Cr}_2\text{O}_7$	0	0.178
		400	0.236
Potassium sulphate. .	K_2SO_4	0	0.1760
Potassium nitrate. . .	KNO_3	0	0.2140
		200	0.267
		300	0.292
Silver chloride. . . .	AgCl	0	0.0848
		200	0.0974
		500	0.101
Silver nitrate.	AgNO_3	50	0.146
Sodium borate.	$\text{Na}_2\text{B}_4\text{O}_7$	45	0.234
Sodium borate (borax).	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	35	0.385
Sodium carbonate. . . .	Na_2CO_3	45	0.256
Sodium chloride.	NaCl	0	0.204
		100	0.217
		400	0.229
		600	0.236
Sodium nitrate.	NaNO_3	0	0.2478
		100	0.294
		250	0.358
Sodium sulphate. . . .	Na_2SO_4	0	0.202
		100	0.220
Water.	H_2O	-40	0.435
(Ice).		0	0.492

Organic Compounds

Cyanamide.	CH_2N_2	20	0.548
Oxalic acid.	$\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	0	0.338
		100	0.416
Tartaric acid.	$\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$	0	0.308
Picric acid.	$\text{C}_6\text{H}_3\text{N}_3\text{O}_7$	0	0.240
		100	0.297
Nitrobenzene.	$\text{C}_6\text{H}_5\text{NO}_2$	20	0.349
Benzene.	C_6H_6	0	0.376
Benzoic acid.	$\text{C}_7\text{H}_6\text{O}_2$	20	0.287
Naphthalene.	C_{10}H_8	0	0.281
		100	0.392
Anthracene.	$\text{C}_{14}\text{H}_{10}$	50	0.308
Palmitic acid.	$\text{C}_{15}\text{H}_{32}\text{O}_2$	0	0.382
Stearic acid.	$\text{C}_{17}\text{H}_{34}\text{O}_2$	15	0.399

TABLE V. (Continued)
*Miscellaneous Solids**

Substance	$t^{\circ}\text{C}$ (Temp. or Range)	C_p
Asbestos.....	20 — 98	0.195
Brass (60% Cu, 40% Zn)	20 — 100	0.0917
Cellulose (dry).....		0.37
Glass		
Crown.....	10 — 50	0.161
Flint.....	10 — 50	0.117
Granite.....	12 — 100	0.192
India rubber (Para).....	? — 100	0.481
Leather (dry).....	0	0.360
Marble.....	0 — 10	0.21
Mica (Mg).....	20 — 98	0.2061
Paraffin.....	0 — 20	0.6939
Porcelain.....	15 — 950	0.26
Vulcanite.....	20 — 100	0.3312
Wood.....		0.42

* From "Handbook of Chemistry and Physics," Hodgman and Lange, Chemical Rubber Publishing Co. (1931), with permission.

LATENT HEAT

Heat of Fusion. The fusion of a crystalline solid at its melting-point to form a liquid at the same temperature is accompanied by an increase in heat content or an absorption of latent heat. Since the volume changes and hence the external work in fusion are small, this heat of fusion is largely utilized in increasing the internal energy content through rearrangement of the atoms. Attempts have been made to establish general relationships between latent heats of fusion and other more easily measured properties. None of these generalizations are accurate, but for the metals it has been found that the atomic heat of fusion is roughly proportional to the absolute temperature of the melting-point, that is,

$$\frac{L_F}{T_F} = 2.2 \quad (38)$$

where

L_F : latent heat of fusion, calories per gram-atom
 T_F : melting temperature, $^{\circ}\text{K}$

Equation (38) may be used for a rough estimate of the heat of fusion of a metal where no experimental data are available. No such generalization has been found to apply to the heats of fusion of chemical compounds.

Experimentally determined values of the latent heats of fusion of a few typical elements and compounds are contained in Table VI. It will be noted that the ratio, L_F/T_F (Equation 38) is far from being constant. Similar data for a great many materials may be found in the International Critical Tables, Vol. V, page 130 (1929).

TABLE VI
LATENT HEATS OF FUSION*

L_F = latent heat of fusion, calories per gram-atom or mol or Chu per pound-atom or mol. To convert to Btu per pound-mol, multiply by 1.8.

t_F = melting-point, °C.

T_F = melting-point, °K.

<i>Elements</i>			
	L_F	t_F	L_F/T_F
Ag.....	2800	961	2.3
Al.....	2340	657	2.5
Cu.....	2650	1083	2.0
Fe*.....	2700	1535	1.5
Na.....	629	98	1.7
Ni.....	4280	1450	2.5
Pb.....	1160	327	1.9
S.....	800	115	0.8
Sn.....	1600	232	3.2
Zn.....	1660	419	2.4

<i>Compounds</i>		
	L_F	t_F
H ₂ O.....	1,435	0.0
Sb ₂ S ₃	5,950	540
CO ₂	2,000	- 58.2
CaCl ₂	6,040	774
NaOH.....	1,600	318
NaCl.....	7,210	804
Carbon tetrachloride.....	640	- 24
Methyl alcohol.....	600	- 97
Acetic acid.....	2,690	16.6
Ethyl alcohol.....	1,150	-114
Benzene.....	2,370	5.4
Aniline.....	1,950	- 7.0
Naphthalene.....	4,550	80
Diphenyl.....	4,020	71
Stearic acid.....	13,500	64

* See also Fig. 63, page 322.

Heat of Transition. Many crystalline substances exhibit *transformation* or *transition-points* at which temperature changes in crystalline structure take place. The equilibrium temperature of transformation is nearly constant although the actual temperature of transformation is frequently a function of the rate at which the substance is heated or

cooled prior to the transformation. The transition usually takes place at a slightly higher temperature when the substance is being heated than when it is being cooled.

Crystalline transformations are accompanied by either absorption or evolution of latent heat. The transformation of the phase which is stable at low temperatures into the phase stable at high temperatures requires an absorption of heat.

Data for the heat absorbed in crystalline transformations have been determined for many substances. A few such data are contained in Table VII. Data for many other substances are included in the section on "Thermochemistry" in the International Critical Tables, Vol. V, page 169 (1929).

TABLE VII
HEATS OF TRANSFORMATION

L_T = heat absorbed in transformation, calories per gram-atom or Chu per pound-atom or mol. To convert to Btu per pound-mol, multiply by 1.8.
 t_T = temperature of transformation, °C.

Data from the International Critical Tables

Transformation	L_T	t_T
Sulphur: rhombic \rightarrow monoclinic	7.0	114–151° C
Iron (electrolytic) (see also Fig. 63, page 322):		
$\alpha \rightarrow \beta$		770
$\beta \rightarrow \gamma$	313	910
$\gamma \rightarrow \delta$	106	1400
Manganese:		
$\alpha \rightarrow \beta$	1325	1070–1130
Nickel:		
$\alpha \rightarrow \beta$	78	320–330
Tin:		
white \rightarrow gray	530	0

HEAT OF VAPORIZATION

The latent heat required to vaporize a substance consists of two parts, the energy absorbed in overcoming the intermolecular forces of attraction in the liquid and the mechanical work performed by the vapors in evolving and expanding against an external pressure. The first energy requirement is known as the heat equivalent of internal work; the latter, the heat equivalent of external work of vaporization. The external work performed by one mol of a substance in vaporizing under a constant pressure is simply equal to the product of the pressure and the increase in volume. Thus,

$$L_{vR} = p(v - v_L) \quad (39)$$

where

$$\begin{aligned} L_{VE} &= \text{external work of vaporization} \\ p &= \text{pressure} \\ v &= \text{volume of vapor} \\ v_L &= \text{volume of liquid} \end{aligned}$$

At ordinary pressures the volume of the liquid may be neglected. If the vapor follows the simple gas law the molal external work of vaporization is equal to RT or approximately $2T$ calories per gram-mol, where T is the temperature of vaporization in degrees Kelvin.

Trouton's Rule. The total latent heat of vaporization is much larger than the latent heat of fusion because the forces of molecular attraction must be overcome to a much greater extent in vaporization than in fusion. According to a rule proposed by Trouton, the ratio of the total molal heat of vaporization, L_v , of a substance at its normal boiling-point to the absolute temperature of the boiling-point T_s is a constant.

$$\text{Thus,} \quad \frac{L_v}{T_s} = K \quad (40)$$

where K is termed Trouton's constant or better, Trouton's ratio. For many substances this ratio is equal to approximately 21 where the latent heat is expressed in calories per gram-mol and the temperature in degrees Kelvin. However, the ratio is by no means a universal constant. In polar liquids (see Chapter III, page 77), Trouton's rule breaks down completely, values of the ratio being much greater than 21. In non-polar liquids the variation is smaller but the ratio increases as the normal boiling-point increases.

The Kistyakowsky Equation. A thermodynamic equation was proposed by Kistyakowsky¹ for the calculation of Trouton's ratio at the normal boiling-point of a non-polar liquid.

$$\frac{L_v}{T_s} = 8.75 + 4.571 \log T_s \quad (41)$$

This equation of Kistyakowsky is a great improvement over Trouton's rule and has been shown to be in excellent agreement with the experimental results for a wide variety of non-polar liquids but is inapplicable to polar liquids such as water and alcohol.

The Clapeyron Equation. A useful relationship between total heat of vaporization and vapor pressure is expressed by the Clapeyron equation, derived from the second law of thermodynamics.

$$\frac{p}{dT} = \frac{1}{T(v_g - v_L)} \quad (42)$$

¹ Zeit. physik. Chem. 107, 65-73 (1923).

where

$$\begin{aligned} p &= \text{vapor pressure at temperature } T \\ L_v &= \text{total molal heat of vaporization} \\ v_g &= \text{molal volume of the vapor} \\ v_L &= \text{molal volume of the liquid} \end{aligned}$$

Equation (42) permits accurate calculation of latent heats of vaporization at any temperature if data for the relationship between vapor pressure and temperature and for the molal volumes of the liquid and vapor are available. This equation is rigorous at all temperatures and pressures. Most of the available values for heats of vaporization at high pressures were calculated in this way from accurate measurements of vapor pressure and specific volume.

Dühring Line Method. At low pressures v_L becomes negligible in comparison to v_g . Assuming that the vapor follows the simple gas law, $v_g = RT/p$, and from (42)

$$\frac{dp}{dT} = \frac{pL_v}{RT^2}$$

By measurement of the slope of the vapor pressure-temperature curve dp/dT is determined and L_v may be calculated directly from Equation (43). This method is very convenient when used in conjunction with Dühring lines to represent the vapor-pressure curve as described in Chapter IV, page 74. The Dühring line relates the temperature, T , at which a substance exerts a vapor pressure, p , to the temperature, T_r , at which a reference substance exerts the same vapor pressure. Applying Equation (43) to the reference substance,

$$\frac{dp}{dT_r} = \frac{L_{vr}}{RT_r^2}$$

where

$$\begin{aligned} L_{vr} &= \text{molal heat of vaporization of the reference} \\ &\quad \text{substance at pressure } p \text{ and temperature } T_r \end{aligned}$$

Combining equations (43) and (44)

$$L_v = L_{vr} \cdot \frac{T_r^2}{T^2} \cdot \frac{dT_r}{dT}$$

The term dT_r/dT is equal to the slope of the Dühring line which is substantially constant. From Equation (45) the heat of vaporization of a substance at any low pressure may be calculated from its Dühring line if data are available for the heat of vaporization of the reference substance at this same pressure. The method is reliable only at low pres-

tures under which the errors of the simple gas law are small. The Dühring lines in Fig. 5 are plotted with water as the reference substance. The heat of vaporization of water at any temperature between 32° and 240° F may be estimated from Fig. 9, page 96.

Illustration 1. Estimate the molal heat of vaporization of ethyl alcohol at a temperature of 40° C.

From Fig. 5 it is seen that at 40° C ethyl alcohol exerts the same vapor pressure as does water at 58° C. The slope of the Dühring line for ethyl alcohol is $\frac{140}{115 + 12}$ 1.10.

From Fig. 9 the heat of vaporization of water at 58° C (136.4° F) is 18,280 Btu per pound-mol.

From Equation (45)

$$L_v = 18,280 \left(\frac{40 + 273}{58 + 273} \right)^2 \times 1.10 = 17,950 \text{ Btu}$$

The experimentally observed value is 17,800 Btu per pound-mol.

TABLE VIII
LATENT HEATS OF VAPORIZATION

l_v = latent heat of vaporization at t° C, calories per gram or Chu per pound.

To convert to Btu per pound multiply by 1.8.

t = temperature, °C.

t_c = critical temperature, °C.

Substance	t		
H ₂ O.....	100	538	374
HCl.....	- 84.3	99	51.4
SO ₂	- 10.1	95	157
NH ₃	- 33.4	327	132
HNO ₃	86	115	
CO ₂	- 56.6	81	31
CS ₂	46.3	84	273
Methyl chloride..	- 23.8	102	143
Methyl alcohol..	64.7	263	240
Acetic acid.....	118.3	96.8	321
Ethyl alcohol...	78.3	204	243
Ethylene glycol..	197	191	
Acetone.....	56.1	125	235
<i>n</i> -propyl alcohol.	97.2	164	264
Ethyl ether.....	34.6	84	194
Aniline.....	183	104	426
Naphthalene....	218	75.5	

Latent heats of vaporization of non-polar substances may be estimated from Equation (41).

The heats of vaporization of a few selected substances are contained in Table VIII. Additional data for many other materials may be found in the International Critical Tables, Vol. V, page 135 (1929).

Effect of Temperature on Heat of Vaporization. The latent heat of vaporization of a substance diminishes as its temperature and pressure are increased. At the critical temperature, as pointed out in Chapter III, the kinetic energies of translation of the molecules become sufficiently great to overcome the potential energies of the attractive forces which hold them together, and molecules can pass from the liquid to the vapor state without additional energization. At the critical point there is no distinction between the liquid and vapor state, either in heat content or other physical properties. Hence, at the critical temperature the latent heat of vaporization becomes equal to zero.

Values of the latent heats of vaporization of several substances have been calculated from Equation (42) for temperatures up to the critical value. However, the necessary data on liquid and vapor volumes are available for only these few materials. The approximate form of the Clapeyron equation (43) permits calculation of the latent heat of vaporization at any temperature from only the vapor-pressure data. However, the equation is rigorous only at low temperatures, corresponding to low pressures at which it may be assumed that the simple gas law is applicable.

A relationship was pointed out by Watson¹ which permits estimation of the latent heat of vaporization at any desired temperature if its value at one temperature is known and if the critical temperature is known. Experimentally determined values of Trouton's ratio, L_v/T , were plotted as ordinates against the ratio of temperature, T , to critical temperature, T_c , both expressed on an absolute scale. This ratio of temperature to critical temperature is termed the *reduced temperature* of a substance. It was found that the curves relating Trouton's ratio to reduced temperature were of similar shape for even widely different types of substances, all converging at the point where the reduced temperature equals unity (the critical temperature), and where the latent heat of vaporization equals zero.

On this basis Fig. 25 was derived relating the correction γ in the following equation to temperature, critical temperature, and boiling-point

$$L = \gamma L_B \cdot \frac{T}{T_B}$$

where

L = latent heat of vaporization at temperature T

T_B = normal boiling-point

L_B = latent heat of vaporization at temperature T_B

¹ Ind. Eng. Chem. **23**, 360 (1931).

By means of Equation (46) it is possible to estimate the latent heat of vaporization of a substance at any temperature if the value at some one temperature is known, together with the critical temperature

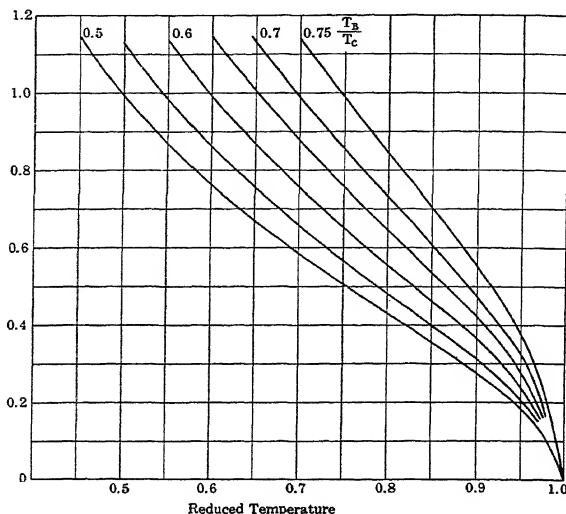


FIG. 25. Temperature Correction to Heat of Vaporization.

Illustration 2. The latent heat of vaporization of ethyl alcohol at its normal boiling-point is 204 calories per gram. The critical temperature is 243°C and the normal boiling-point 78°C . Estimate the latent heat of vaporization at a temperature of 180°C .

	351	0.680
Reduced temperature at $180^{\circ}\text{C} = \frac{453}{516}$		0.880
γ (from Fig. 25) =		0.50
From Equation (46)		

$$L = 0.50 \times 204 \times \frac{453}{351} = 132 \text{ cal per gram}$$

The observed value is 136 calories per gram.

For normal or non-polar liquids no experimental data are necessary for the prediction of latent heats of vaporization. Equation (41) of Kistyakowsky may be used to obtain the value at the normal boiling-point. Values at other temperatures may then be obtained from Equa-

tion (46). If the critical temperature is not known it may be estimated from the liquid density, molecular weight, and boiling-point by means of Equation (5), Chapter IV, page 78.

Although Equation (41) is applicable only to non-polar substances, no such limitation applies to Equation (46). It was found that such polar substances as water, ethyl alcohol, and ammonia are in good agreement with the average curves.

Effect of Pressure on Latent Heat of Vaporization. In the preceding discussion of latent heat of vaporization it has been considered that vaporization takes place under a total pressure equal to the vapor pressure of the liquid. This will be true only if the vapors are evolved undiluted by other gases or vapors. The increase in total pressure resulting from the presence of other gases above the surface of a vaporizing liquid is known to have a marked effect on the latent heat of vaporization. However, this effect is negligible when pressures are low with correspondingly low concentrations of molecules in the vapor phase. For all ordinary industrial purposes it is permissible to neglect the effect of total pressure on heat of vaporization when conditions are such that deviations from the simple gas law are not large. In other words, under such conditions it is assumed that when a liquid vaporizes into a gas the heat absorbed is the same as though the liquid were vaporizing in contact with only its own vapors and under a total pressure equal to its vapor pressure.

In dealing with high-pressure processes the effect of total pressure on heat of vaporization may be of considerable importance. Under such conditions of close proximity of molecules and large intermolecular attractive forces it is natural to expect that the presence of other gases would greatly affect the internal energy of the vapors and the energy change accompanying vaporization. These effects would result from the same factors which contribute to the effect of total pressure on vapor pressure as discussed in Chapter IV, page 79.

The experimental data on the effects of total pressure on heat of vaporization are rather scattered and contradictory. In general it would be expected that increase in total pressure would diminish the latent heat of vaporization. However, this action would depend entirely on the specific nature of the gases present, as does the effect of total pressure on vapor pressure. It may be considered that the presence of a highly compressed gas exerts a solvent action on a liquid, the nature of the effect depending on the natures of all the components of the system as well as on the pressures. With the increasing importance of high-pressure processes it is to be expected that reliable data will be obtained on this effect for many of the more important liquid-gas systems.

CALCULATION OF HEAT CONTENT

As pointed out on page 108, the total heat or energy content of matter is unknown. However, the heat content of a given substance relative to some reference state can be calculated from its thermophysical properties. This state can be taken arbitrarily as a temperature of 0°C (32°F), atmospheric pressure, and the state of aggregation normally existent at this temperature and pressure. The reference state for steam is usually taken as the liquid state, under its own vapor pressure, at 0°C .

Hereafter the term heat content or enthalpy as used in this book will be identical with total relative heat content or total relative enthalpy.

The enthalpy of a substance is calculated as the change in enthalpy in passing from the reference state to the existing conditions. As previously pointed out, at constant pressure the increase in enthalpy is equal to the heat absorbed. Ordinarily at moderate pressures the effect of pressure on the enthalpy of liquids and solids may be neglected except when conditions are close to the critical point. This subject is discussed in Chapter XIII.

Illustration 3. Calculate the heat content of 1 lb of steam at a temperature of 350°F and a pressure of 50 lb per sq in., referred to the liquid state at 32°F .

Solution. From the vapor-pressure data of water (Fig. 6) it is found that the saturation temperature under an absolute pressure of 50 lb per sq in. (2585 mm of Hg) is 138°C or 281°F . The steam is therefore superheated 69°F above its saturation temperature. The relative heat content will be the heat absorbed in heating 1 lb of liquid water from 32°F to 281°F , vaporizing it to form saturated steam at this temperature, and heating the steam at constant pressure to a temperature of 350°F . The total heat content will be the sum of the sensible heat of the liquid, the latent heat of vaporization, and the superheat of the vapors. The effect of pressure on the enthalpy of the liquid water at 32°F is neglected.

The mean specific heat of water between 32°F and 281°F is 1.006. The mean heat capacity of water vapor between 281°F and 350°F at a pressure of 50 lb per sq in. is 9.2 Btu per lb-mol per $^{\circ}\text{F}$. The latent heat of vaporization of water at 281°F is 926.0 Btu per lb.

Sensible heat of liquid water at 281°F = $(281 - 32)$	
1.006 =	250.3 Btu per lb
Latent heat of vaporization at 281°F	926.0 Btu per lb
Superheat of vapor = $(350 - 281) \frac{9.20}{18}$ =	35.2 Btu per lb
Heat content =	1211.5 Btu per lb

Extensive steam tables have been compiled giving the heat contents of steam under widely varying conditions, all with respect to a standard reference state. Table IX is an abridged table giving the properties of saturated steam over the range from 32° to 500°F . Similar tables are available for the properties of superheated steam. In calcu-

TABLE IX
PROPERTIES OF SATURATED STEAM*

Pressure		Temp. °F	Volume cu ft per lb	Heat content of liquid in Btu	Latent heat of vaporiza- tion in Btu	Internal energy of vaporiza- tion in Btu
Lb per sq in. abs	In. of mercury					
<i>P</i>	<i>p</i>	<i>t</i>	<i>V</i>	<i>q</i>	<i>l_v</i>	<i>l_{ti}</i>
0.0982	0.2	34.55	2992	2.56	1071.7	1016.3
0.1965	0.4	52.67	1550	20.75	1062.0	1005.7
0.2947	0.6	63.98	1056	32.06	1056.0	998.4
0.3929	0.8	72.35	805	40.42	1051.5	993.0
0.4912	1.0	79.06	652	47.11	1047.9	988.7
0.589	1.2	84.68	549	52.72	1044.9	985.0
0.688	1.4	89.54	474.3	57.57	1042.3	919.9
0.786	1.6	93.83	418.2	61.84	1040.0	979.1
0.884	1.8	97.67	374.3	65.68	1037.9	976.6
0.982	2.0	101.17	338.9	69.16	1036.0	974.3
1.965	4.0	125.44	176.5	93.37	1022.5	958.3
2.947	6.0	140.80	120.7	108.69	1013.9	948.1
3.929	8.0	152.26	92.1	120.2	1007.4	940.4
4.912	10.0	161.50	74.8	129.4	1002.1	934.1
5.894	12.0	169.30	63.0	137.2	997.5	928.8
6.88	14.0	176.06	54.6	143.9	993.6	924.1
7.86	16.0	182.06	48.14	149.9	990.0	920.0
8.84	18.0	187.46	43.12	155.4	986.7	916.2
9.82	20.0	192.38	39.08	160.3	983.8	912.7
10.81	22.0	196.89	35.75	164.8	981.1	909.6
11.79	24.0	201.09	32.95	169.0	978.5	906.6
12.77	26.0	205.00	30.57	173.0	976.1	903.8
13.75	28.0	208.67	28.53	176.6	973.8	901.2
14.70	29.92	212.00	26.81	180.0	971.7	898.8
Lb per sq in. gauge						
15	0.3	213.0	26.30	181.0	971.2	898.1
20	5.3	228.0	20.10	196.0	961.7	887.3
25	10.3	240.1	16.32	208.2	953.8	878.4
30	15.3	250.3	13.76	218.6	947.1	870.7
35	20.3	259.3	11.91	227.7	941.0	863.9
40	25.3	267.2	10.51	235.8	935.5	857.8
45	30.3	274.4	9.41	243.1	930.5	852.2
50	35.3	281.0	8.53	249.8	925.9	847.1
55	40.3	287.1	7.80	255.9	921.5	842.3
60	45.3	292.7	7.18	261.7	917.4	837.8
65	50.3	298.0	6.66	267.1	913.5	833.5
70	55.3	302.9	6.22	272.2	909.8	829.5
75	60.3	307.6	5.82	277.0	906.2	825.6

* From "Properties of Steam and Ammonia" by G. A. Goodenough.

NOTE. The total heat energy of one pound of dry saturated steam equals $q + l_v$; and the total internal energy, $q + l_{ti}$.

TABLE IX. (Continued)

Pressure		Temp. °F	Volume cu ft per lb	Heat content of liquid in Btu	Latent heat of vaporiza- tion in Btu	Internal energy of vaporiza- tion in Btu
Lb per sq in. abs	Lb per sq in. gauge					
<i>P</i>	<i>p</i>	<i>t</i>	<i>V</i>	<i>q</i>	<i>l_v</i>	<i>l_{si}</i>
80	65.3	312.0	5.48	281.6	902.8	821.9
85	70.3	316.3	5.18	286.0	899.6	818.4
90	75.3	320.3	4.905	290.1	896.4	815.0
95	80.3	324.1	4.663	294.1	893.4	811.7
100	85.3	327.8	4.442	297.9	890.5	808.6
105	90.3	331.4	4.240	301.6	887.6	805.5
110	95.3	334.8	4.057	305.1	884.8	802.6
115	100.3	338.1	3.889	308.6	882.1	799.7
120	105.3	341.3	3.735	311.9	879.5	796.9
125	110.3	344.4	3.593	315.1	876.9	794.2
130	115.3	347.4	3.461	318.2	874.4	791.6
135	120.3	350.3	3.340	321.2	872.0	789.0
140	125.3	353.1	3.226	324.2	869.6	786.4
145	130.3	355.8	3.120	327.0	867.2	784.0
150	135.3	358.5	3.020	329.8	864.9	781.6
155	140.3	361.1	2.927	332.5	862.7	779.2
160	145.3	363.6	2.839	335.2	860.5	776.9
165	150.3	366.1	2.757	337.8	858.3	774.6
170	155.3	368.5	2.679	340.3	856.2	772.4
175	160.3	370.8	2.605	342.8	854.1	770.2
180	165.3	373.1	2.536	345.2	852.0	768.0
185	170.3	375.4	2.470	347.6	849.9	765.9
190	175.3	377.6	2.408	350.0	847.9	763.9
195	180.3	379.7	2.348	352.2	846.0	761.8
200	185.3	381.9	2.292	354.5	844.0	759.8
205	190.3	383.9	2.238	356.7	842.1	757.8
210	195.3	386.0	2.186	358.8	840.2	755.9
215	200.3	388.0	2.137	361.0	838.3	754.0
220	205.3	390.0	2.090	363.0	836.5	752.1
225	210.3	391.9	2.045	365.1	834.6	750.2
230	215.3	393.8	2.002	367.1	832.8	748.3
235	220.3	395.6	1.961	369.1	831.0	746.5
240	225.3	397.5	1.921	371.0	829.3	744.7
245	230.3	399.3	1.883	373.0	827.5	742.9
250	235.3	401.1	1.846	374.9	825.8	741.2
260	245.3	404.5	1.777	378.6	822.4	737.7
270	255.3	407.9	1.713	382.2	819.1	734.4
280	265.3	411.2	1.654	385.7	815.8	731.1
300	285.3	417.5	1.545	392.4	809.4	724.7
400	385.3	444.8	1.162	422.0	780.6	695.9
500	485.3	467.2	0.928	446.6	755.0	670.9
600	585.3	486.5	0.770	468.0	731.8	648.5

lating these tables it is necessary to take into account the variation of the heat capacity with pressure, as discussed in Chapter XIII. From such tables of heat contents, the absorption of heat accompanying a change of conditions under a constant pressure is readily calculated as the difference between the heat contents at the final and initial conditions. Tables and charts of heat contents have been worked out for a number of substances for which frequent thermal calculations are made in engineering practice. Such data for irons and metallurgical slags are contained in Fig. 63, page 322, and for benzol in Fig. 89, page 432.

Calculations of heat content often include several changes of state. For example, in calculating the heat content of zinc vapor at 1000° C and atmospheric pressure, relative to the solid at standard conditions, it is necessary to include the sensible heat content of the solid metal at the melting-point, the latent heat of fusion, the sensible heat absorbed in heating the liquid from the melting-point to the normal boiling-point, the latent heat of vaporization, and the sensible heat absorbed in heating the zinc vapor from the boiling-point up to 1000° C at constant pressure.

Illustration 4. Calculate the heat content of zinc vapor at 1000° C and atmospheric pressure, relative to the solid at 0° C. Zinc melts at 419° C and boils under atmospheric pressure at 907° C.

The mean heat capacities of the solid and liquid may be estimated from Fig. 22, page 127.

Mean specific heat of solid, 0° C to 417° C = 0.105

Mean specific heat of liquid, 419° C to 907° C = 0.109

From Table VI, page 134, the latent heat of fusion is 1660 calories per gram-atom.

The latent heat of vaporization at the normal boiling-point may be estimated from Equation (41).

$$L_v/1180 = 8.75 + 4.571 \log 1180 = 22.80$$

$$L_v = 26,900 \text{ calories per gram-mol}$$

Since zinc vapor is monatomic its molal heat capacity at constant pressure is constant and equal to 4.98 calories per gram-mol (Table I), page 113.

Sensible heat absorbed by solid = $0.105 (419 - 0) =$ 44 calories per gram

Latent heat of fusion = $\frac{1660}{65.4} =$ 25 calories per gram

Sensible heat absorbed by liquid =

$0.109 (907 - 419) =$ 53 calories per gram

Latent heat of vaporization = $\frac{26,900}{65.4} =$ 412 calories per gram

Sensible heat absorbed by vapor = $\frac{4.98}{65.4} (1000 - 907) =$ 7 calories per gram

Total relative heat content 541 calories per gram

Frequently it is difficult to determine experimentally the individual heats of transition involved in heating a substance. Under such conditions the heat content is measured directly and tabulated as such for various temperatures. For example, the heat content of steel at various temperatures is determined by cooling in a calorimeter from these initial temperatures. This determination includes all heats of transition undergone in the cooling process. Steel undergoes so many transformations in cooling and the changes in thermal properties during these changes are known with so small a degree of accuracy that calculations of heat contents are frequently inaccurate. Furthermore, experimental values of the heat content of steel will vary with the method of cooling, owing to the fact that the final state of this solid is dependent upon the rate of cooling. To be correct, the heat content of such a metal should be stated with respect to its composition and metallographic structure in the final solid state.

HEAT CONTENT OF HUMID AIR

The properties of humid air are conveniently expressed on the basis of the weight of humid air which contains either 1 pound or 1 pound-mol of moisture-free air. The heat content of the quantity of humid air containing a unit quantity of moisture-free air is the sum of the sensible heat content of the dry air and the total heat content of the water vapor which is associated with it. The reference states ordinarily chosen are gaseous air and liquid water at 0° C. The water vapor in the air may be considered as derived from liquid water at 0° C by the following series of processes:

1. The liquid water is heated to the dew-point of the humid air.
2. The water is vaporized at the dew-point temperature to form saturated vapor.
3. The water vapor is superheated to the dry-bulb temperature of the air.

The heat content of the water will be the sum of the sensible heat absorbed by the liquid, the heat of vaporization at the dew-point, and the superheat absorbed by the vapor.

Illustration 5. Calculate the heat content, per pound of dry air, of air at a pressure of 1 atmosphere, a temperature of 100° F, and having a percentage humidity of 50%.

Solution. From the humidity chart, Fig. 9, page 96, is seen that air under these conditions contains 0.0345 mol of water per mol of dry air or $\frac{0.0345(18)}{29} = 0.0215$ lb of water per pound of dry air. This corresponds to a dew-point of 79° F.

From Fig. 13, page 117, the mean molal heat capacity of water vapor between 79° F and 100° F is 8.37 and that of oxygen and nitrogen between 32° F and 100° F is 6.95.

The heat of vaporization at 79° F may be estimated from Fig. 9 as 18,840 Btu per lb-mol or 1046 Btu per lb.

Sensible heat content of air = $(100 - 32) \frac{6.95}{29.0} = \dots\dots$	16.3 Btu
Sensible heat of liquid water = $(79 - 32) 0.0215 = \dots\dots$	1.0 Btu
Latent heat of water = $1046 \times 0.0215 = \dots\dots\dots$	22.5 Btu
Superheat of water vapor = $(100 - 79) \times 0.0215 \times \frac{8.37}{18} = \dots\dots\dots$	0.2 Btu
Total relative heat content.....	40.0 Btu per lb of dry air

Humid Heat of Air. It has been frequently pointed out that when dealing with humid air it is convenient to use 1 pound or 1 pound-mol of dry air as the basis of calculations, regardless of the humidity of the air. In problems dealing with the heating or cooling of air where no change in moisture content takes place the total change in heat content is equal to the sum of the change in the sensible heat content of the dry air and the change in sensible heat content of the water vapor. For example, in heating 1 pound of dry air associated with H pounds of water vapor from t_1 to t_2 degrees Fahrenheit, the total heat, q , required is given by the equation,

$$q = C_{pa}(t_2 - t_1) + H(C_{pw})(t_2 - t_1) \quad (47)$$

where

C_{pa} = the mean specific heat of air at constant pressure

C_{pw} = the mean specific heat of water vapor at constant pressure

Instead of considering the air and water vapor separately it is convenient to employ a heat capacity term which combines the two.

Thus,
$$q = S(t_1 - t_2) \quad (48)$$

where

S = heat capacity of one pound of dry air and of the water associated with it, expressed in Btu per pound of dry air per degree F

Combining (47) and (48)

$$(49)$$

The combined heat capacity, S , is termed the *humid heat capacity* of the air. Over the low temperature range from 30° to 180° F the mean heat capacity of dry air is 0.240 Btu per lb and that of water vapor is 0.466 Btu per lb, as estimated from Fig. 13, page 117. Accordingly the

humid heat capacity of air when expressed in Btu per pound of air per degree Fahrenheit is given by the equation,

$$S = 0.240 + 0.466 H \quad (50)$$

Adiabatic Humidification. In the discussion of the humidity chart, Chapter IV, page 96, it was pointed out that a line of constant wet-bulb temperature also represents the relationship between dry-bulb temperature and humidity in the adiabatic vaporization of water into air. This relationship may be derived from the thermophysical data of the system and is used in locating the wet-bulb temperature lines on the humidity chart. The same procedure may be used to establish wet-bulb temperatures in any other system of liquid and gas in which it is known that the wet-bulb temperature does not change appreciably during adiabatic vaporization. The derivation is as follows:

When air is cooled by the adiabatic vaporization of water into it, sensible heat is derived from the humid air to supply the heat necessary in vaporizing the water at the wet-bulb temperature and in heating the evolved vapor to the existing dry-bulb temperature. Since the total heat content of the system remains constant, the heat lost by the humid air must equal that gained by the water in vaporization and superheating. This equality may be expressed mathematically for the evaporation of dH mols of water into humid air containing 1 mol of dry air. Thus,

$$dH[L_v + c_{pw}(t - t_w)] = -S dt \quad (51)$$

where,

H = molal humidity.

L_v = molal heat of vaporization at temperature t_w .

c_{pw} = mean molal heat capacity of water vapor.

t = dry-bulb temperature.

t_w = temperature of adiabatic evaporation.

S = mean molal humid heat capacity of air.

Assuming that the wet-bulb temperature remains constant, as humidification proceeds the final dry-bulb temperature reached by the entire weight of air will be the wet-bulb temperature t_w , corresponding to saturation and a humidity H_w . In the temperature range from 32° to 200° F the molal heat capacities of air and water vapor may be taken from Fig. 13 as constant at 6.95 and 8.4, respectively. Then, from Equation (49), $S = 6.95 + 8.4H$. Substituting these values in Equation (51) and rearranging,

$$\frac{dH}{6.95 + 8.4H} = \frac{dt}{L_v + 8.4(t - t_w)} \quad (52)$$

Integrating between the limits H, t and H_w, t_w ,

$$\frac{1}{8.4} \ln \frac{6.95 + 8.4H}{6.95 + 8.4H_w} = \frac{1}{8.4} \ln \frac{L_v}{L_v + 8.4(t - t_w)}$$

$$\text{or} \quad 6.95 L_v + 8.4 L_v H + 8.4(t - t_w)(6.95 + 8.4H) = 6.95 L_v$$

$$\text{or} \quad t = \frac{(H_w - H)L_v}{6.95 + 8.4H} \quad (53)$$

The temperature, t_w , of adiabatic evaporation corresponds to the experimental value of wet-bulb temperature provided evaporation from the wet-bulb thermometer proceeds adiabatically, that is, with no gain or loss of heat by radiation, and also provided the actual vapor-pressure equilibrium is established at the liquid-air interface. The first condition is realized where the air is passed rapidly over the wet-bulb thermometer such that radiation errors become negligible; the second condition is true where the rate of evaporation by diffusion keeps pace with the rate of heat transfer by convection. This latter condition is realized without appreciable error at temperatures below 150° F. *The lines of adiabatic evaporation are therefore commonly referred to as wet-bulb temperature lines and will be so designated.*

The adiabatic cooling or wet-bulb temperature lines of Fig. 9 were constructed from Equation (53). Corresponding to a selected value of t_w , values of dry-bulb temperature were calculated to correspond to various humidities, thus establishing a complete curve. The wet-bulb temperature lines of Fig. 9 which apply to gases of appreciable carbon dioxide content were constructed from a similar equation in which the effect of the carbon dioxide on the humid heat capacity of the gas was considered. The molal heat capacity of carbon dioxide may be assumed to be constant at about 9.3 (from Fig. 13). Then,

$$S = 6.95(1 - x) + 9.3x + 8.4H$$

where

x = mol fraction of CO_2 in the dry gas

With this modification Equation (53) becomes

$$t = \frac{(H_w - H)L_s}{6.95(1 - x) + 9.3x + 8.4H} + t_w$$

This equation permits calculations of adiabatic cooling or wet-bulb temperature lines to apply to combustion gases or other mixtures containing appreciable amounts of carbon dioxide.

PROBLEMS

1. Calculate the heat equivalent, in Btu, of the work required to compress isothermally 1000 cu ft of air at a temperature of 80° F and a barometric pressure of 29 in. of Hg to a final gauge pressure of 150 lb per sq in. Assume the applicability of the simple gas law.

2. From the equations of Table I, page 113, calculate the mean heat capacity of nitrogen.

- In Calories per kilogram per degree Centigrade from 0° to t° C.
- In Chu per pound per degree Centigrade from 0° to t° C.
- In Calories per cubic meter per degree Centigrade from 0° to t° C.
- In Btu per pound-mol per degree Fahrenheit from 32° to t° F.
- In Btu per pound per degree Fahrenheit from 32° to t° F.
- In Btu per cubic foot per degree Fahrenheit from 32° to t° F.
- In Calories per kilogram per degree Centigrade from 1000° to 2000° C.
- In Btu per pound per degree Fahrenheit from 1000° to 2000° F.
- Calculate the heat capacity of nitrogen in Calories per kilogram per degree Centigrade at 1500° C.

3. Calculate the amount of heat given off when 1 cu m of air (standard conditions) cools from 500° to -100° C at a constant pressure of 1 atmosphere, assuming the heat capacity formulas of Table I, page 113, to be valid over this temperature range.

4. Calculate the number of Calories required to heat, from 200° to 1200° C, 1 cu m (standard conditions) of a gas having the following composition by volume:

CO ₂	20%
N ₂	77%
O ₂	2%
H ₂	1%

5. (Postpone to Chapter XIII.) Calculate the number of Btu required to heat 10 lb of air from a temperature of 0° to 300° C under the following constant pressures:

- 0.1 atmosphere.
- 1.0 atmosphere.
- 50 atmospheres.
- 100 atmospheres.

6. Calculate the number of Btu required to heat 1 lb each of the following liquid from a temperature 32° to 100° F.

- Acetone.
- Carbon tetrachloride.
- Ether.
- Propyl alcohol.

7. Calculate the number of calories required to heat 1000 grams of each of the following aqueous solutions from 0° to 100° C.

- 5% NaCl by weight.
- 20% NaCl by weight.
- 20% H₂SO₄ by weight.
- 20% KOH by weight.
- 20% NH₄OH by weight.
- 20% Pb(NO₃)₂ by weight.

8. The following tables contain data on the specific heats of solutions of various concentrations. Calculate the partial heat capacities in calories per gram of each component at each of the indicated concentrations. Plot these results against percentage composition over the indicated concentration ranges as in Fig. 21.

- Heat capacities of solutions of sucrose (C₁₂H₂₂O₁₁) (cane sugar) in water at 20° C. (Use method of tangent slope.)

Per cent sucrose by weight	Heat capacity calories per gram $-^{\circ}$ C
5	0.965
10	0.930
15	0.901
20	0.870
30	0.810
40	0.750
50	0.703
60	0.676

- b. Heat capacities of aqueous HCl solutions at 60° C. (Use method of tangent slope.)

Mol fraction of HCl	Heat capacity calories per gram — °C
0.000.....	1.000
0.0476.....	0.881
0.0909.....	0.782
0.130.....	0.710
0.167.....	0.669
0.200.....	0.640
0.231.....	0.622
0.259.....	0.610

- c. Heat capacities of solutions of ethyl alcohol (C_2H_5OH) in benzene (C_6H_6) at 20° C. (Use method of tangent intercepts.)

Mol fraction of ethyl alcohol	Heat capacity calories per gram — °C
0.000.....	0.406
0.158.....	0.430
0.298.....	0.459
0.421.....	0.485
0.530.....	0.504
0.629.....	0.520
0.718.....	0.531
0.798.....	0.540
0.872.....	0.556
0.938.....	0.560
1.000.....	0.575

9. Calculate the specific heat at 20° C of MgO , SiO_2 (quartz), CaO , CuO , PbO from Kopp's rule and compare with the experimental values.

10. Calculate the heat equivalent in Btu of the external work of vaporization of 1 lb of water at a temperature of 80° F, assuming that water vapor follows the simple gas law.

11. Calculate the total latent heat of vaporization in Btu per pound of diethyl ether ($C_2H_5OC_2H_5$) at its normal boiling temperature by the following methods:

a. From the equation of Kistyakowsky.

b. From the Dühring line of Fig. 5.

12. From its Dühring line estimate the latent heat of vaporization in Btu per pound of aniline ($C_6H_5NH_2$) under a pressure of 100 mm of Hg.

13. Obtaining the necessary boiling-point and critical data from Fig. 3, estimate the total latent heat of vaporization, in Btu per pound, of *n*-octane (C_8H_{18}) when boiled under a pressure of 200 lb per sq in.

14. Diphenyl ($C_6H_5 \cdot C_6H_5$) is a non-polar compound having a normal boiling-point of 255° C. By assuming its coefficient of thermal expansion to be similar to that of naphthalene it is estimated that the density of liquid diphenyl at its boiling-point is 0.75 gram per cubic centimeter. From the data of the text estimate:

a. The critical temperature of diphenyl.

b. The boiling-point of diphenyl under a pressure of 40 lb per sq in.

c. The latent heat of vaporization in Btu per pound of diphenyl boiled under a pressure of 40 lb per sq in.

15. Calculate the latent heat of vaporization, in calories per gram, of water at a temperature of 100°C by means of the Clapeyron equation. At this temperature $dp/dt = 27.17$, where p is the vapor pressure in millimeters of mercury and t is the temperature in degrees Centigrade.

16. The vapor pressure of zinc in the range from 600° to 985°C is given by the equation

$$\log p = -\frac{6160}{T} + 8.10$$

where

p = vapor pressure, millimeters of mercury

T = temperature, degrees K

Estimate the latent heat of vaporization of zinc at 907°C , the normal boiling-point. Compare this result with that calculated from the equation of Kistyakowsky.

17. From the International Critical Tables obtain the following data:

- a. The heat capacity, in calories per gram per degree C, of
 1. Liquid *o*-nitroaniline ($\text{C}_6\text{H}_7\text{N}_2\text{O}_2$) at 100°C .
 2. Liquid SiCl_4 at 25°C .
 3. A solution containing 50 mol per cent ether ($\text{C}_4\text{H}_{10}\text{O}$) in benzene (C_6H_6) at a temperature of 20°C .
 4. Solid FeS_2 at 100°C .
- b. The heat of fusion of
 1. BaCl_2
 2. Benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$).
 3. Stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$).
- c. The total latent heat of vaporization of
 1. Nitrogen at -202°C .
 2. SiCl_4 at 57°C .
 3. *n*-octyl alcohol ($\text{C}_8\text{H}_{18}\text{O}$) at 196°C .

18. Calculate the total heat content in Calories per kilogram referred to the solid at 0°C , of molten copper at a temperature of 1200°C .

19. Obtaining the latent heat data from the steam tables, calculate the total heat content, in Btu per pound, relative to the liquid at 32°F , of steam at a temperature of 500°F which is superheated 200°F above its saturation-point.

20. Calculate the total heat content in Btu per pound relative to 32°F , of pure molten iron at a temperature of 2850°F . In heating iron from 32°F to its melting-point it undergoes three transformations, from α to β , from β to γ , and from γ to δ forms.

21. Using the latent heat data calculated in Problem 14, calculate the total heat content, in Btu per pound relative to the solid at 32°F , of saturated diphenyl vapors under a pressure of 40 lb per sq in.

22. Calculate the total heat content, in Btu per pound of dry air relative to air and liquid water at 32°F , of humid air at a temperature of 150°F , a pressure of 1 atmosphere, and having a percentage humidity of 40%.

23. Humid air at a pressure of 1 atmosphere has a dry-bulb temperature of 180°F and a wet-bulb temperature of 120°F . This air is cooled to a dry-bulb temperature of 115°F . Calculate the heat evolved, in Btu per pound of dry air.

24. Hot gases are passing through a chimney at a rate of 1200 cu ft per minutes, measured at the existing conditions of 600°C and a pressure of 740 mm of Hg. The gases have the following composition by volume on the dry basis.

CO_2	12%
N_2	80%
O_2	8%

The dew-point of the gases is 50°C and they contain 20 grams of carbon soot per cubic meter measured at the chimney conditions. Calculate the total heat content of the material passing through the chimney per minute, in Btu relative to gases, solid carbon, and liquid water at 18°C .

CHAPTER VI

THERMOCHEMISTRY AT STANDARD CONDITIONS

STANDARD HEAT OF REACTION

All chemical reactions are accompanied either by an absorption or by an evolution of energy which usually manifests itself as heat. *Thermochemistry* is a branch of physical chemistry which deals with the changes of heat content accompanying chemical reactions.

As pointed out in Chapter V the total energy content of a substance is dependent upon its temperature, pressure and state of aggregation and is independent of the means by which these conditions were brought about. Likewise the total change in internal energy, ΔE , of a system which results from any physical change or chemical reaction depends only on the initial and final states of all the reactants and products in the system. The total change in energy will be the same whether or not it is absorbed or evolved in the form of heat, radiant energy, electrical energy, work, or other forms.

From Equation (1), Chapter V

$$\Delta E = q - w_f - w_e \quad (1)$$

where

ΔE = increase in total internal energy

q = heat absorbed

w_f = electrical and radiant energy evolved by system

w_e = work of expansion done by the system

In addition to a change in internal energy during a chemical reaction there may also be a change in the pressure and volume of the system. The change in the product pV is dependent only upon the initial and final states of the system. The corresponding change in enthalpy is given by Equation (5), page 108.

$$\Delta H = \Delta E + \Delta(pV) \quad (2)$$

It follows that the change in heat content or enthalpy is also dependent only upon the initial and final states of the system.

Combining Equations (1) and (2)

$$\Delta H = \Delta E + \Delta(pV) = q - w_f - w_e + \Delta(pV) \quad (3)$$

Thus, the enthalpy change accompanying any physical or chemical process, although it is determined by the initial and final conditions and is independent of the course of the change, may be calculated by a summation of the quantities of heat, work, electrical and radiant energies evolved together with the change in pV .

As stated previously, the term heat content is used interchangeably with enthalpy. Because of its general use the term heat content will be continued with the understanding that it has the same broad significance as enthalpy.

Heat of Reaction. It is customary in industrial thermochemical calculations to designate the evolution of heat as positive. Accordingly, the decrease in heat content during a chemical reaction is known as the *heat of reaction* and is designated by the symbol Q_p . Hence,

$$Q_p = -\Delta H_p$$

The heat of reaction accompanying a chemical change is dependent not only on the chemical nature of each reacting material and product but also on their physical states. For purposes of organizing thermochemical data it is convenient to define a *standard heat of reaction* which may be recorded as a characteristic of the reaction and from which heats of reaction under other conditions may be calculated. The most commonly accepted standard heat of reaction is defined as the change in heat content resulting from the procedure of the reaction under a pressure of 1 atmosphere, starting and ending with all materials at a temperature of 18° C.

For example, 1 gram-atom (65.38 grams) of zinc may be allowed to react with 2073 grams of 1.0 molal aqueous hydrochloric acid containing 2.0 gram-mols of HCl. The reaction may be carried out in a calorimeter under atmospheric pressure with all reactants at an initial temperature of 18° C. During the course of the reaction the system will become heated, hydrogen gas will be evolved, and a 0.5 molal solution of zinc chloride will be formed. When the reaction is completed the resultant solution and the hydrogen gas may be cooled to 18° C. If no evaporation of water takes place it will be found that 34,230 calories will be evolved by the system. The net result of the reaction is the conversion of 2 mols of hydrochloric acid in aqueous solution into 1 mol of zinc chloride in aqueous solution and 1 mol of hydrogen gas at atmospheric pressure, all at a temperature of 18° C. The measured amount of heat represents the standard molal heat of reaction for this particular reaction, proceeding under atmospheric pressure in an aqueous solution of the specified concentration.

Exactly the same net result may be produced by allowing the above

reaction to proceed in an electrolytic cell in which one electrode is zinc and the other platinum. An electric motor might be connected to the cell and be permitted to do work as the reaction proceeds. In this case the amount of heat evolved will be less than 34,230 calories by the heat equivalent of the electrical energy produced by the cell. However, the heat of reaction is the same and equal to the sum of the amounts of energy evolved as heat and as electrical energy.

Conventions and Symbols. As pointed out in the preceding section, the heat of reaction accompanying a chemical change is dependent on the physical state of each reactant and product as well as on its chemical nature. For this reason, in order to define a heat of reaction it is necessary to specify completely the nature and state of each material. The following system of conventions and symbols, to be used in conjunction with the conventional chemical equation, will be adopted for this purpose.

The formula of a substance appearing in an equation will designate not only the nature of the substance but also the quantity of it which is involved in the reaction. Thus, H_2SO_4 indicates 1 mol of sulphuric acid, and $1\frac{1}{2} \text{ N}_2$ indicates $1\frac{1}{2}$ mols of nitrogen. All equations will be written with the reactants on the left-hand and the products on the right-hand side. The value of the heat of reaction accompanying an equation will be the heat of reaction resulting from the procedure of the reaction from the left to the right of the equation *as written*. If the reaction were to proceed in the reverse direction the heat of reaction would be of opposite sign.

Unless otherwise specified it will be assumed that each reactant or product is in its normal state of aggregation at a temperature of 18°C and a pressure of 1 atmosphere.

The state of aggregation of a substance will be indicated by a letter in parentheses following its chemical formula. Thus (g) indicates the gaseous state, (l) the liquid, and (s) the solid.

Additional information may accompany these letters in parentheses. Thus, S (rhombic) and C (diamond) indicate sulphur in the rhombic state and carbon as diamond, respectively, while S (monoclinic) and C (graphite) indicate monoclinic sulphur and solid graphitic carbon. In the case of a gas the pressure may be specified. Thus, CO_2 (g, 2 atm) indicates gaseous carbon dioxide under a pressure of two atmospheres.

The concentration of a substance in aqueous solution will be indicated by its molality (M), by the number of mols of solvent (n_1) per mol of solute, or by the mol fraction of the solute (N_2). Thus, ($M = 0.1$) following a chemical formula indicates that the substance is in aqueous solution with a molality of 0.1. The symbol ($n_1 = 200$) indicates an aqueous solution with 200 mols of water per mol of solute. The symbol ($N_2 = 0.55$) indicates an aqueous solution in which the mol fraction of

the solute is 0.55. In the case of a highly dilute aqueous solution, such that additional dilution produces no thermal effect, the symbol (*aq*) follows the formula of the solute.

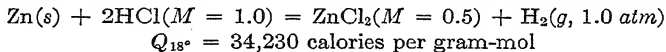
The concentration of a substance in non-aqueous solution is indicated by the above symbols, accompanied in the parentheses by the formula of the solvent. Thus, ($\text{C}_2\text{H}_6\text{O}, N_2 = 0.55$) indicates that a substance is in alcoholic solution with a mol fraction of 0.55.

Ionic reactions will be indicated in the usual manner, for example H^+ and Ca^{++} for the positive hydrogen and calcium ions and Cl^- and SO_4^{--} for the negative chloride and sulphate ions, respectively.

As previously pointed out, positive values of Q will represent an evolution of heat, that is, a decrease in heat content, or $Q = -\Delta H$. Where the initial and final temperature of the system is constant a subscript may be used with Q (or ΔH) to designate this temperature. The heat of reaction also may be indicated by writing the number of units of heat evolved as one of the products of the reaction.

When heat is evolved in a reaction, corresponding to a decrease in heat content (positive Q , negative ΔH), the reaction is termed *exothermic*; when heat is absorbed the reaction is said to be *endothermic*.

With the aid of the above symbols the states of a chemical reaction may be completely indicated by the equation. For example, the equation



completely designates the changes occurring in the reaction which was described in the preceding section.

Heat of Formation. The *heat of formation* of a chemical compound is a special case of the standard heat of a chemical reaction wherein the reactants are the necessary elements and the compound in question is the only product formed. Heats of formation are always expressed with reference to a standard state. The molal heat of formation of a compound will represent, unless otherwise stated, the total heat of reaction, Q , when 1 mol of the compound is formed from the elements in a reaction beginning and ending at 18°C and at a pressure of 1 atmosphere with the reacting elements originally in the states of aggregation which are stable at these conditions of temperature and pressure. The heat of formation of a compound is positive when its formation from the elements is accompanied by a decrease in heat content. A compound whose heat of formation is positive is termed an *exothermic compound*. If the heat of formation is negative it is called an *endothermic compound*.

For example, the molal heat of formation of liquid water is $+68,310$ calories per gram-mol. This means that when 2.016 grams of hydrogen gas combine with 16 grams of oxygen at a temperature of 18°C and a

pressure of 1 atmosphere to form 18.016 grams of liquid water at the same temperature, the heat given off to the surroundings is 68,310 calories. It is obvious that this reaction will not proceed at a constant temperature but during its progress will be at a very high temperature and the product formed will be temporarily in the vapor state. However, upon cooling to 18° C this sensible and latent heat appearing temporarily in the system itself will be evolved and included in the heat of formation. Similarly any energy manifesting itself as light will be included in the heat of formation. If water vapor were the final product at 18° C the heat of formation would be less by an amount equal to the total latent heat of vaporization of water at 18° C. The molal heat of formation of water vapor at 18° C is 57,750 calories. The heat of vaporization of water at 18° C is accordingly 10,560 calories per mol or 597 calories per gram.

Fully 95 per cent of the inorganic compounds are exothermic. Thus, most chemical compounds contain less internal energy than the elements from which they are formed. Heat must always be supplied in the reduction of metals from their ores, as in the metallurgy of copper, iron, zinc, lead, and tin. Conversely, heat is given off in the oxidation of the elements, as in the combustion of carbon and sulphur. The number of endothermic compounds is relatively small, particularly among the inorganic compounds. Among the endothermic compounds are included many of the nitrides, cyanides, ferrocyanides, carbides, hydrides, oxides of nitrogen, and a few compounds of gold. For example, mercurous nitride, sulphur nitride, cadmium cyanide, nickel cyanide, Prussian blue, carbon disulphide, hydrogen iodide, hydrogen selenide, nitric oxide, and gold oxide are endothermic compounds.

The basic thermochemical data of inorganic compounds are generally presented in terms of standard heats of formation. In the International Critical Tables, Vol. V, page 169, are extensive tables giving the heats of formation of a great variety of inorganic compounds, both in pure states and in solutions of varying concentrations. When a compound is hydrated the heat of formation in this table includes the heat of formation of the water making up the hydrate. This convention is not followed in other similar tables.

In Table X are a few selected values of heats of formation, calculated for the most part from the data of the International Critical Tables. In the third column the state of each compound is indicated. In the fourth column are heats of formation of the compounds in the indicated states. These values are expressed in Calories per gram-mol, Calories per kilogram-mol, or Chu per pound-mol. To convert to Btu per pound-mol these values should be multiplied by 1.8.

TABLE X
HEATS OF FORMATION AND SOLUTION
Reference Conditions: 18° C and 1 atmosphere pressure

Units

calories per gram-mol, or Calories per kilogram-mol, or Chu per pound-mol.
Data from International Critical Tables, Vol. V, page 169 (1929), unless otherwise indicated.

Abbreviations

c = crystalline state.

s = solid.

l = liquid.

g = gas.

dil = dilute solution.

∞ = infinite dilution.

ppt = precipitated solid.

amorph = amorphous state.

Compound	Formula	State	Heat of Formation	Mols of Water	Heat of Solution
Acetic acid.....	CH ₃ COOH	<i>l</i>	117,500	200	358
Aluminum chloride.....	AlCl ₃	<i>c</i>	166,000	600	77,600
Aluminum hydroxide.....	Al(OH) ₃	<i>ppt</i>	304,500		
Aluminum nitride.....			131,430		
Aluminum oxide.....	Al ₂ O ₃		399,000		
Aluminum silicate.....	Al ₂ O ₃ · SiO ₂	sillimanite	554,000		
Aluminum disilicate.....	Al ₂ O ₃ · 2SiO ₂	<i>amorph</i>	979,000		
Aluminum disilicate.....	Al ₂ O ₃ · 2SiO ₂ · 2H ₂ O		944,000		
Trialuminum disilicate.....	3Al ₂ O ₃ · 2SiO ₂		1,464,000		
Aluminum sulphate.....			714,000	∞	169,300
Ammonia.....	NH ₃		10,940	200	8,480
Ammonia.....	NH ₃	<i>l</i>	15,830	200	3,580
Ammonium carbonate.....	(NH ₄) ₂ CO ₃	<i>dil</i>	223,000		
Ammonium bicarbonate.....	NH ₄ HCO ₃		203,000	400	-6,520
Ammonium chloride.....	NH ₄ Cl		75,100	∞	-3,800
Ammonium hydroxide.....	NH ₄ OH		86,500		
Ammonium nitrate.....	NH ₄ NO ₃		88,000	∞	-6,470
Ammonium oxalate.....			267,000	400	-7,900
Ammonium sulphate.....	(NH ₄) ₂ SO ₄		277,500	400	-2,360
Ammonium acid sulphate.....	NH ₄ HSO ₄		240,000	800	+550
Antimony trioxide.....	Sb ₂ O ₃		165,400	∞	-37,000
Antimony pentoxide.....	Sb ₂ O ₅		231,000	∞	-2,860
Antimony sulphide.....			35,600		
Arsenic acid.....			215,000	∞	-406
Arsenic trioxide.....	As ₂ O ₃	octahedral	154,000	∞	-5,500
Arsenic pentoxide.....	As ₂ O ₅		218,000	∞	+6,000
Barium acetate.....	Ba(C ₂ H ₃ O ₂) ₂		358,000	∞	+5,250
Barium carbonate.....	BaCO ₃	<i>ppt</i>	291,000		
Barium carbonate.....	BaCO ₃	<i>c</i>	283,000 ⁽¹⁾		
Barium chlorate.....	Ba(ClO ₃) ₂		174,000	200	-6,700
Barium chloride.....	BaCl ₂		205,000	2000	+2,200
Barium chloride.....	BaCl ₂ · 2H ₂ O		349,000	2000	-4,800
Barium hydroxide.....	Ba(OH) ₂		225,800	400	+11,650
Barium oxide.....	BaO		133,000	∞	+36,100
Barium peroxide.....	BaO ₂		151,700		
Barium silicate.....	BaSiO ₃	<i>glass</i>	358,000		
Barium sulphate.....	BaSO ₄	<i>ppt</i>	345,500	∞	-5,970
Barium sulphide.....	BaS		111,000	∞	+7,400
Bismuth oxide.....	Bi ₂ O ₃		135,500		
Boric acid.....	H ₃ BO ₃		251,500	∞	-5,500
Boron oxide.....	B ₂ O ₃		280,000	∞	+7,400
Bromine chloride.....	BrCl		700 ⁽¹⁾		

⁽¹⁾ "Handbook of Chemistry and Physics," Hodgman and Lange, Chemical Rubber Publishing Co. (1931).

TABLE X. — *Continued*

Compound	Formula	State	Heat of Formation	Mols of Water	Heat of Solution
	CdCl_2		93,000	400	+3,080
	CdO		65,200		
	CdSO_4		218,000	400	+10,680
cadmium sulphide....	CdS		38,900		
	$\text{Ca}_2(\text{C}_2\text{H})$		357,500		+6,830
		glass	549,000		
Calcium aluminate.....	Al_2O_3	glass	692,000		
Calcium aluminate.....	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	glass	836,000		
Calcium aluminum silicate.....			1,485,000		
Calcium aluminum silicate.....	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2$		781,000		
Calcium carbide.....	CaC_2		14,580		
Calcium carbonate.....	CaCO_3	<i>ppt</i>	288,000		
Calcium carbonate.....	CaCO_3	calcite	289,000		
Calcium chloride.....	CaCl_2		190,500		+17,950
Calcium chloride.....	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$		623,500		-4,470
Calcium fluoride.....	CaF_2	<i>ppt</i>	286,000		
Calcium hydroxide.....	$\text{Ca}(\text{OH})_2$	<i>c</i>	236,000		+2,680
Calcium nitrate.....	$\text{Ca}(\text{NO}_3)_2$		225,000	400	+3,820
Calcium oxalate.....	CaC_2O_4	<i>ppt</i>	333,000		
Calcium oxide.....	CaO		151,700		+18,650
Calcium phosphate.....	$\text{Ca}_3(\text{PO}_4)_2$		982,000		
Calcium silicate.....	$\text{CaO} \cdot \text{SiO}_2$	glass	375,000		
Calcium silicate.....	$2\text{CaO} \cdot \text{SiO}_2$	glass	432,000		
Calcium sulphate.....	CaSO_4		338,000		+2,650
Calcium sulphide.....	CaS		113,500		+6,210
Carbon β -graphite.....	C		0		
Diamond.....	C	<i>c</i>	-167		
Gas carbon.....	C	<i>amorph</i>	-478		
Charcoal (H-free).....	C	<i>amorph</i>	-478		
Coke.....	C	<i>amorph</i>	-2,600		
Sugar carbon.....	C	<i>amorph</i>	-2,389		
Carbon monoxide.....	CO	<i>g</i>	26,780(2)		+3,440
Carbon dioxide.....	CO_2	<i>g</i>	94,400		+4,750
Carbon disulphide.....	CS_2	<i>g</i>	-28,670		
Carbon disulphide.....	CS_2	<i>l</i>	-21,980		
Carbon tetrachloride.....	CCl_4	<i>g</i>	35,900		
Carbon tetrachloride.....	CCl_4	<i>l</i>	33,800		
Chloric acid.....	HClO_3	<i>dil</i>	19,100		
Chromium chloride (ic).....	CrCl_3		139,500		30,570
Chromium chloride(ous).....	CrCl_2		99,600		18,620
Chromium oxide.....	Cr_2O_3		276,720		
Chromium oxide.....	Cr_2O_3	<i>amorph</i>	266,200		
Chromium trioxide.....	CrO_3		136,000	80	2,435
Cobalt oxide.....	CoO		57,600		
Cobalt oxide.....			192,500		
Cobalt sulphide.....	CoS	<i>ppt</i>	19,800		
Copper acetate.....	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	<i>c</i>	214,500	∞	+2,389
Copper carbonate.....	CuCO_3	<i>ppt</i>	141,400		
Copper chloride.....	CuCl_2		51,400	800	+11,180
Copper chloride.....	CuCl		32,500		
Copper oxide.....	CuO		34,900		
Copper oxide.....	Cu_2O		39,900		
Copper sulphate.....	CuSO_4		178,600	800	+15,900
Copper sulphide.....	CuS		11,600		
Copper sulphide.....	Cu_2S		18,950		
Copper nitrate.....	$\text{Cu}(\text{NO}_3)_2$		72,400	200	+10,390

(2) Rossini, F. D., Bureau of Standards Journal of Research, 6, 1-35 (1931).

TABLE X. — *Continued*

Compound	Formula	State	Heat of Formation	Mols of Water	Heat of Solution
Cyanogen.....			-70,700		+6,800
Hydrobromic acid.....	HBr	<i>g</i>	8,650		+19,930
Hydrochloric acid.....	HCl	<i>g</i>	22,050		+17,500
Hydrocyanic acid.....	HCN	<i>g</i>	-30,100		+6,210
Hydrofluoric acid.....	HF	<i>l</i>	+70,900	600	+4,730
Hydriodic acid.....	HI	<i>g</i>	-5,930		+19,250
Hydrogen oxide.....	H ₂ O	<i>g</i>	57,740		
Hydrogen oxide.....	H ₂ O	<i>l</i>	68,310 ^(*)		
Hydrogen peroxide.....	H ₂ O ₂	<i>l</i>	44,500	200	+454
Hydrogen sulphide.....	H ₂ S	<i>g</i>	5,250		+4,610
Iron acetate.....	Fe(C ₂ H ₃ O ₂) ₂	<i>dil</i>	357,000		
Iron carbonate.....	FeCO ₃		185,000		
Iron chloride.....	FeCl ₃		196,300	1000	31,780
Iron hydroxide.....	Fe(OH) ₃	<i>ppt</i>	197,200		
Iron oxide.....	Fe ₂ O ₃	<i>c</i>	191,600		
Iron oxide.....	FeO	<i>c</i>	64,000		
Iron oxide.....	Fe ₃ O ₄	magnetite	267,000		
Iron silicate.....	FeO · SiO ₂		264,800		
Iron sulphate.....	Fe ₂ (SO ₄) ₃	<i>dil</i>	640,000		
Iron sulphate.....	FeSO ₄		217,000	400	14,700
Iron sulphide.....	FeS		23,050		
Iron sulphide.....	FeS ₂	pyrites	35,800		
Lead acetate.....	Pb(C ₂ H ₃ O ₂) ₂	<i>c</i>	233,900		+1,468
Lead carbonate.....	PbCO ₃		168,800		
Lead chloride.....	PbCl ₂		85,600		-6,540
Lead nitrate.....	Pb(NO ₃) ₂		108,400	400	-7,620
Lead oxide.....	PbO		52,450		
Lead peroxide.....	PbO ₂		62,580		
Lead suboxide.....	Pb ₂ O		51,200		
Lead sesquioxide.....			174,000		
Lead sulphate.....	PbSO ₄		214,500		
Lead sulphide.....	PbS	<i>ppt</i>	22,200		
Lithium chloride.....	LiCl		97,350		+8,600
Lithium hydroxide.....	LiOH		116,300		+4,630
Magnesium carbonate.....	MgCO ₃		267,500		
Magnesium chloride.....	MgCl ₂		153,000	800	+36,000
Magnesium hydroxide.....	Mg(OH) ₂	<i>ppt</i>	213,600		
Magnesium oxide.....	MgO	amorph (?)	145,000		
Magnesium silicate.....	MgSiO ₃		348,300		
Magnesium sulphate.....	MgSO ₄		301,000	400	+20,250
Manganese carbonate.....	MnCO ₃	<i>ppt</i>	208,100		
Manganese chloride.....	MnCl ₂	<i>c</i>	112,600	400	18,500
Manganese oxide.....	MnO	<i>c</i>	90,800		
Manganese oxide.....	Mn ₂ O ₄	<i>c</i>	328,000		
Manganese dioxide.....	MnO ₂	<i>c</i>	125,400		
Manganese dioxide.....	MnO ₂	amorph	119,400		
Manganese silicate.....	MnO · SiO ₂	<i>c</i>	300,000		
Manganese silicate.....	MnO · SiO ₂	glass	291,000		
Manganese sulphate.....		<i>c</i>	247,000	400	13,900
Manganese sulphide.....	MnS	<i>ppt</i>	47,300		
Manganese sulphide.....	MnS		59,700		
Mercury acetate.....	Hg(C ₂ H ₃ O ₂) ₂		198,000		-4,060
Mercury chloride.....	HgCl ₂		53,400		-3,250
Mercury chloride.....	Hg ₂ Cl ₂	<i>ppt</i>	63,000		
Mercury nitrate.....	Hg(NO ₃) ₂	<i>dil</i>	58,000		
Mercury nitrate.....			207,300		

(*) Bureau of Standards, Journal of Research, 7, 330 (1931), gives latest value as 68,280.

TABLE X. — *Continued*

Compound	Formula	State	Heat of Formation	Mols of Water	Heat of Solution
Mercury oxide.....	HgO		21,750		
Mercury oxide.....	Hg ₂ O		21,500		
Mercury sulphate.....	HgSO ₄		162,400		
Mercury sulphate.....			171,600		
Mercury sulphide.....	HgS	<i>amorph</i>	10,500		
Mercury thiocyanate.....	Hg(CNS) ₂		-50,400		
Molybdenum dioxide.....	MoO ₂		131,300		
Molybdenum trioxide.....	MoO ₃		173,800		
Nickel cyanide.....	Ni(CN) ₂		-23,250		
Nickel hydroxide.....	Ni(OH) ₂	<i>ppt</i>	+196,500		
Nickel hydroxide.....	Ni(OH) ₂	<i>ppt</i>	+129,700		
Nickel oxide.....	NiO		+57,800		
Nickel sulphide.....	NiS	<i>ppt</i>	+20,800		
Nickel sulphate.....	NiSO ₄	<i>dil</i>	+227,000		
Nitrogen oxide.....	NO		-21,600		
Nitrogen oxide.....	N ₂ O		-16,950		
Nitrogen oxide.....	N ₂ O		-18,720		
Nitrogen pentoxide.....	N ₂ O ₅		+12,000		
Nitrogen pentoxide.....	N ₂ O ₅		+14,560	400	16,670
Nitrogen tetroxide.....			-1,860		
Nitrogen trioxide.....	N ₂ O ₃		-21,400 ⁽¹⁾		
Nitric acid.....	HNO ₃ · 2H ₂ O		+42,450	∞	+7,430
Oxalic acid.....			340,000	300	-8,580
Oxalic acid.....			197,000	∞	-2,530
Perchloric acid.....	HClO ₄		19,350	500	+20,300
Permanganic acid.....	HMnO ₄	<i>dil</i>	123,200		
Phosphoric acid (meta).....	HPO ₃		225,000	∞	9,600
Phosphoric acid (ortho).....	H ₂ PO ₄		301,000	400	5,420
Phosphoric acid (pyro).....			529,000	∞	10,220
Phosphorous acid (hypo).....	H ₂ P ₂ O ₄		139,000	450	2,389
Phosphorous acid (ortho).....	H ₂ PO ₃		225,800	∞	2,820
Phosphorous trichloride.....	PCl ₃		70,000	1000	+72,000
Phosphorous pentoxide.....	P ₂ O ₅		366,000		
Platinum chloride.....	PtCl ₂		62,550		+19,350
Platinum chloride.....	PtCl ₄		17,000 ⁽¹⁾		
Potassium acetate.....			174,600	400	+3,350
Potassium carbonate.....	K ₂ CO ₃		275,000	400	+6,500
Potassium chlorate.....	KClO ₃		89,800		-10,500
Potassium chloride.....	KCl		104,300		-4,420
Potassium chromate.....	K ₂ CrO ₄		329,500	800	-5,210
Potassium cyanide.....	KCN		28,200	200	-3,100
Potassium dichromate.....	K ₂ Cr ₂ O ₇		481,800		-18,350
Potassium fluoride.....	KF		134,000	400	+4,110
Potassium oxide.....	K ₂ O		86,200	300	+75,000
Potassium sulphate.....			338,500		-6,700
Potassium sulphide.....			88,100		+22,450
Potassium sulphite.....	K ₂ SO ₃		268,000	600	+1,430
Potassium thiosulphate.....	K ₂ S ₂ O ₃ · H ₂ O		336,000		-6,200
Potassium hydroxide.....	KOH		102,000		+12,840
Potassium nitrate.....	KNO ₃		118,800		-8,670
Potassium permanganate.....	KMnO ₄		194,200	1000	-10,390
Selenium oxide.....	SeO ₂		56,400		
Silicon carbide.....	SiC		1,430		
Silicon tetrachloride.....	SiCl ₄	<i>l</i>	149,000		
Silicon tetrachloride.....	SiCl ₄	<i>g</i>	142,600		
Silicon dioxide.....	SiO ₂	<i>quartz</i>	201,000		

TABLE X. — *Continued*

Compound	Formula	State	Heat of Formation	Mols Water	Heat of Solution
Silver bromide.....	AgBr	<i>c</i>	23,850		
Silver chloride.....	AgCl	<i>c</i>	30,580	∞	-14,000
Silver nitrate.....	AgNO ₃	<i>c</i>	30,200	400	-5,450
Silver sulphide.....	Ag ₂ S	<i>c</i>	5,020		
Sodium acetate.....	NaC ₂ H ₃ O ₂	<i>c</i>	171,000	400	+3,940
Sodium arsenate.....		<i>c</i>	350,000	500	+23,200
Sodium tetraborate.....		<i>c</i>	742,000	∞	+10,250
Sodium borax.....	10H ₂ O	<i>c</i>	1,460,000	1600	-25,850
Sodium bromide.....	NaBr	<i>c</i>	86,200	200	-191
Sodium carbonate.....	Na ₂ CO ₃	<i>c</i>	270,400	400	+5,610
Sodium carbonate.....	Na ₂ CO ₃ · 10H ₂ O	<i>c</i>	976,000	400	-16,390
Sodium bicarbonate.....	NaHCO ₃	<i>c</i>	227,200	400	-4,200
Sodium chlorate.....	NaClO ₃	<i>c</i>	82,350	∞	-5,280
Sodium chloride.....	NaCl	<i>c</i>	98,300	∞	-1,280
Sodium cyanide.....	NaCN	<i>c</i>	22,900	200	-481
Sodium fluoride.....	NaF	<i>c</i>	136,200	∞	-548
Sodium hydroxide.....	NaOH	<i>c</i>	101,900	∞	+10,120
Sodium iodide.....	NaI	<i>c</i>	69,400	200	+1,410
Sodium nitrate.....	NaNO ₃	<i>c</i>	112,400	∞	-5,120
Sodium oxalate.....		<i>c</i>	316,000	1500	-5,500
Sodium oxide.....	Na ₂ O	<i>c</i>	99,100	∞	56,400
Sodium triphosphate.....	Na ₃ PO ₄	<i>c</i>	447,000	900	+24,200
Sodium diphosphate.....	Na ₂ HPO ₄	<i>c</i>	414,500	600	+5,640
Sodium monophosphate.....	NaH ₂ PO ₄	<i>dil</i>	355,000 ⁽¹⁾		
Sodium phosphite.....	Na ₂ HPO ₃	<i>c</i>	335,000	∞	+9,130
Sodium selenate.....	Na ₂ SeO ₄	<i>c</i>	261,400	400	0
Sodium selenide.....	Na ₂ Se	<i>c</i>	69,500	∞	+18,640
Sodium sulphate.....	Na ₂ SO ₄	<i>c</i>	326,300	∞	+358
Sodium sulphate.....	Na ₂ SO ₄ · 10H ₂ O	<i>c</i>	1,030,000	400	-18,900
Sodium bisulphate.....	NaHSO ₄	<i>c</i>	265,000	800	+1,670
Sodium sulphide.....	Na ₂ S	<i>c</i>	89,800	400	+15,350
Sodium sulphide.....		<i>c</i>	417,500	1000	-5,000
Sodium sulphite.....	Na ₂ SO ₃	<i>c</i>	259,000	800	+2,630
Sodium bisulphite.....	NaHSO ₃	<i>dil</i>	206,800		
Sodium silicate.....	Na ₂ SiO ₃	<i>glass</i>	369,000		
Sodium silico fluoride.....	Na ₂ SiF ₆	<i>c</i>	661,000	∞	-2,390
Sulphur dioxide.....	SO ₂	<i>g</i>	69,400	2000	8,560
Sulphur trioxide.....	SO ₃	<i>g</i>	91,500	∞	49,200
Sulphuric acid.....		<i>l</i>	189,750	∞	20,500
Tellurium oxide.....		<i>c</i>	78,300	∞	-1,840
Tin chloride(ic).....	SnCl ₄	<i>l</i>	127,300	250	29,900
Tin chloride(ous).....	SnCl ₂	<i>c</i>	81,100	300	358
Tin oxide(ic).....	SnO ₂	<i>c</i>	138,000		
Tin oxide(ous).....	SnO	<i>c</i>	69,750		
Titanium oxide.....	TiO ₂	<i>amorph</i>	214,000		
Titanium oxide.....	TiO ₂	<i>c</i>	217,300		
Tungsten oxide.....	WO ₃	<i>c</i>	126,100		
Vanadium oxide.....		<i>c</i>	437,200		
Zinc acetate.....		<i>c</i>	261,200	720	9,800
Zinc carbonate.....		<i>ppt</i>	193,200		
Zinc chloride.....	ZnCl ₂	<i>c</i>	99,500	600	15,710
Zinc hydroxide.....	Zn(OH) ₂	<i>amorph</i>	153,500		
Zinc oxide.....	ZnO	<i>c</i>	84,300		
Zinc sulphate.....	ZnSO ₄	<i>c</i>	229,500	400	18,550
Zinc sulphide.....	ZnS	<i>c</i>	459,800		
Zirconium oxide.....	ZrO ₂	<i>glass</i>	178,600		

When a compound is hydrated, the heat of formation in this table includes the heat of formation, from the elements, of the water forming the hydrate. For example, the heat of formation of solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is given as 623,500. This represents the heat of reaction accompanying the formation at 18°C of 1 mol of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ from solid calcium and gaseous chlorine, hydrogen, and oxygen.

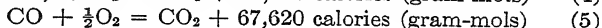
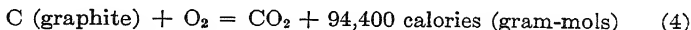
In the sixth column of Table X are values of the heats of solution of some of the compounds. The general subject of heats of solution will be discussed in a later section. These values in Table X merely represent the heat of reaction which results from the formation of a solution of the specified concentration from 1 mol of the compound and the number of mols of liquid water indicated in the fifth column. By means of these values the total heats of formation of the dissolved materials may be calculated. For example, in the case of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, mentioned above, the heat of solution in 400 mols of water is -4470 . The heat of formation of the undissolved $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is 623,500. The total heat of formation of 1 gram-mol of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in solution in 400 gram-mols of water is the sum of these two values, $623,500 + (-4470)$, or 619,030 calories.

If an element normally exists in more than one allotropic form at 18°C and atmospheric pressure, one of these forms is selected to serve as the basis of heats of formation throughout the table. This is equivalent to assigning a heat of formation of zero to the element in the particular form selected. For example, carbon may exist as graphite, diamond, or amorphous carbon. The β -graphite form has been selected as the basis of the heats of formation of all carbon compounds. This is indicated by presenting the heat of formation of β -graphite as zero in the table. On this basis all other forms of elementary carbon have negative heats of formation. The heat of formation, for example, of barium carbonate is the heat of reaction accompanying the formation of the compound from graphite and the other necessary elements. When more than one allotropic form of an element exists, the particular form on which the tables are based can be identified as the form whose heat of formation is given as zero.

Laws of Thermochemistry. At a given temperature and pressure the quantity of energy required to decompose a chemical compound into its elements is precisely equal to that evolved in the formation of that compound from its elements. This principle was first formulated by Lavoisier and Laplace in 1780. For example, the heat of formation of sodium chloride is 98,300 calories. Theoretically the same amount of energy will be required to decompose sodium chloride into sodium and chlorine.

A corollary of this first principle of thermochemistry is known as the law of constant heat summation, which states that the total heat of reaction of a chemical process is the same whether the reaction takes place in one or several steps. The total change in heat content of a system is dependent upon the temperature, pressure, state of aggregation, and state of combination at the beginning and at the end of the reaction and is independent of the number of intermediate chemical reactions involved. This principle is known as the law of Hess, formulated in 1840.

By means of this principle it is possible to calculate the heat of formation of a compound from a series of reactions not involving the direct formation of the compound from the elements. The majority of chemical compounds cannot be prepared in the pure state directly from the elements. For example, the heat of formation of carbon monoxide cannot be measured directly because it cannot be prepared in a pure state from the elements without the concomitant formation of carbon dioxide. However, pure carbon dioxide may be formed from its elements and the heat of reaction measured. Also, pure carbon monoxide may be oxidized to form carbon dioxide and the heat of this reaction measured. Thus, at 18° C,



From the law of Hess, the heat of formation of carbon monoxide will be the same as the net heat of reaction accompanying (a) the formation of carbon dioxide from the elements and (b) the decomposition of this carbon dioxide into carbon monoxide and an element, oxygen. The first step is represented by Equation (4) with a heat of reaction of +94,400. The second step is the reverse of the reaction of Equation (5) with a heat of reaction of -67,620. The net heat of reaction of the two processes is the sum, 94,400 - 67,620 or +26,780 calories, the heat of formation of carbon monoxide.

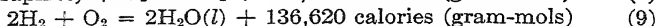
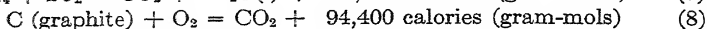
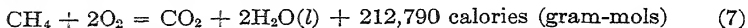
The result of this application of the law of Hess is exactly the same as that obtained by treating Equations (4) and (5) as algebraic equalities and combining them as such. If Equation (5) is subtracted from (4),



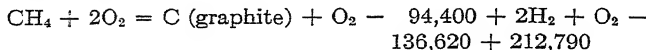
All thermochemical equations may be treated in this manner and combined with each other according to the rules of algebra. In this way it is possible to use the principle of Hess effectively in calculating the heat of a reaction for a complicated series of reactions. The heat

of formation of any compound may be calculated if the heat of any one reaction into which it enters is known together with the heat of formation of each of the other compounds present in the reaction.

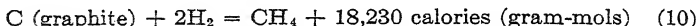
For example, it is practically impossible to measure directly the heats of formation of the hydrocarbons. However, a hydrocarbon may be oxidized completely to carbon dioxide and water and this heat of reaction measured. The heat of formation of the hydrocarbon may then be calculated from the heats of formation of the other compounds present in the reaction, carbon dioxide and water. Thus,



Solving (8) and (9) for CO_2 and H_2O , respectively, and substituting these values in (7),



or



By the principle of constant heat summation it is thus possible to calculate heats of reaction which cannot be determined by direct measurement. For example, the oxidation of linseed oil and the souring of milk are reactions which proceed very slowly. By measuring the heats of combustion of the initial reactants and final products it is possible to calculate the desired heat of reaction. Similarly the heat of transition of a compound to an allotropic form such as graphite to diamond may be impossible to measure directly. However, the difference between the heats of combustion of these two forms of carbon will give the desired heat of transition. This method will be very inexact when the heats of combustion are extremely large compared with the heat of transition.

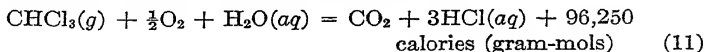
Standard Heat of Combustion. The heat of combustion of a substance is the heat of reaction resulting from the oxidation of the substance with elementary oxygen. All experimental thermochemical data on organic compounds are ordinarily expressed in terms of the heats of combustion of the respective compounds. These data are not necessarily the results of combustion experiments but may be indirectly obtained from measurements of other heats of reaction which will lead to greater accuracy. Heats of combustion data are available for many substances which are ordinarily non-combustible, for example, carbon tetrachloride.

The usually accepted *standard heat of combustion* is that resulting from combustion of a substance, in the state which is normal at 18° C and atmospheric pressure, with the combustion beginning and ending at a temperature of 18° C. The data ordinarily presented for standard heats of combustion correspond to final products of combustion which are in their normal states at a temperature of 18° C and at a pressure of 1 atmosphere. The major final products will generally be gaseous carbon dioxide and liquid water.

The standard heat of combustion of a substance is dependent on the extent to which oxidation is carried. Unless otherwise specified, a value of standard heat of combustion corresponds to complete oxidation of all carbon to carbon dioxide and of all hydrogen to liquid water. Where other oxidizable elements are present it is necessary to specify the extent to which the oxidation of each is carried in designating a heat of combustion. For example, in oxidizing an organic chlorine compound, either gaseous chlorine or hydrochloric acid may be formed, depending on the conditions of combustion. If sulphur is present its final form may be either the dioxide or the trioxide.

The situation is further complicated by the fact that such products may form aqueous solutions with the water which is also a product of combustion. Standard heats of combustion of compounds which contain elements such as S, Cl, I, Br, N, and F must always be accompanied by complete specification of the final state of each product.

In Table XI are a few selected values of standard heats of combustion of organic compounds. These values, in all cases, correspond to the formation of gaseous carbon dioxide from all carbon present in the compound. The hydrogen in the original compound forms liquid water or may be utilized, in part, to form mineral acids when such elements as Cl, S, or N are present. The final products of combustion which are formed from other elements are specifically designated. For example, the heat of combustion of gaseous chloroform is given as 96,250 calories per gram-mol. In the heading of this section of the table dealing with halogen derivatives the final state of chlorine is specified as HCl in dilute aqueous solution. Therefore, the heat of combustion of chloroform corresponds to the heat of the following reaction:



From the heat of combustion of a substance its heat of formation may be calculated if the heat of formation of each of the other products entering into the combustion reaction is known. Thus, in order to calculate the heat of formation of chloroform from Equation (11) it is

TABLE XI
 STANDARD HEATS OF COMBUSTION

Reference conditions: 18° C, 1 atmosphere pressure

$$Q_{18} = -\Delta H_{18}$$

Data from International Critical Tables, Vol. V, page 162 (1929), unless otherwise indicated.

Units

calories per gram-mol. Calories per kilogram-mol. Chu per pound-mol.

Abbreviations

s = solid.

l = liquid.

g = gaseous.

Hydrocarbons

Final Products: CO₂(g), H₂O(l).

Compound	Formula	State	Heat of Combustion
Carbon (graphite)	C	s	94,400
Carbon (coke)....	C	s	97,000
Carbon monoxide.	CO	g	67,620 ⁽¹⁾
Hydrogen.....	H ₂	g	68,310 ⁽¹⁾
Methane.....	CH ₄	g	212,790 ⁽¹⁾
Acetylene.....	C ₂ H ₂	g	312,000
Ethylene.....	C ₂ H ₄	g	332,000
Ethane.....	C ₂ H ₆	g	372,810 ⁽²⁾
Allylene.....	C ₃ H ₄	g	464,600
Propylene.....	C ₃ H ₆	g	490,200
Trimethylene.....	C ₃ H ₈	g	496,800
Propane.....	C ₃ H ₈	g	530,570 ⁽²⁾
Isobutylene.....	C ₄ H ₈	g	647,200
Isobutane.....	C ₄ H ₁₀	g	686,310 ⁽²⁾
n-butane.....	C ₄ H ₁₀	g	687,940 ⁽²⁾
Amylene.....	C ₆ H ₁₀	l	803,400
Cyclopentane.....	C ₅ H ₁₀	l	783,600
Isopentane.....	C ₅ H ₁₂	g	844,700 ⁽²⁾
Isopentane.....	C ₅ H ₁₂	l	838,300
n-pentane.....	C ₅ H ₁₂	g	845,370 ⁽²⁾
Benzene.....	C ₆ H ₆	g	787,200
Benzene.....	C ₆ H ₆	l	783,400
Hexalene.....	C ₆ H ₈	l	952,600
Cyclohexane.....	C ₆ H ₁₂	l	939,000
n-hexane.....	C ₆ H ₁₄	l	990,600
Toluene.....	C ₇ H ₈	l	936,000
Cycloheptane.....	C ₇ H ₁₄	l	1,087,300
n-heptane.....	C ₇ H ₁₆	l	1,149,000
o-xylene.....	C ₈ H ₁₀	l	1,093,000
m-xylene.....	C ₈ H ₁₀	l	1,089,600
p-xylene.....	C ₈ H ₁₀	l	1,089,100
n-octane.....	C ₈ H ₁₈	l	1,305,000
Mesitylene.....	C ₉ H ₆	l	1,243,600
Naphthalene.....	C ₁₀ H ₈	s	1,231,800
Camphene.....	C ₁₀ H ₁₆	s	1,468,000
Decane.....	C ₁₀ H ₂₂	l	1,610,200
Diphenyl.....	C ₁₂ H ₁₀	s	1,493,600
Anthracene.....	C ₁₄ H ₁₀	s	1,695,000
Phenanthrene.....	C ₁₄ H ₁₀	s	1,693,000
Hexadecane.....	C ₁₆ H ₃₄	s	2,559,000

⁽¹⁾ Rossini, F. D. Bureau of Standards Journal of Research **7**, 330 (1931), gives latest corrected values as 67,595, 63,280, and 212,550, respectively.

⁽²⁾ Rossini, F. D. Bureau of Standards Journal of Research **12**, 735-50 (1934).

TABLE XI. — *Continued**Alcohols**Final Products: CO₂(g), H₂O(l).*

Compound	Formula	ate	Heat of Combustion
Methyl alcohol.....	CH ₃ O	l	170,900
Ethyl alcohol.....	C ₂ H ₅ O	l	328,000
Glycol.....	C ₂ H ₆ O ₂	l	281,900
Allyl alcohol.....	C ₃ H ₅ O	l	442,400
n-propyl alcohol.....	C ₃ H ₇ O	l	482,000
Isopropyl alcohol.....	C ₃ H ₈ O	l	474,800
Glycerol.....	C ₃ H ₈ O ₃	l	379,000
n-butyl alcohol.....	C ₄ H ₁₀ O	l	639,000
Amyl alcohol.....	C ₅ H ₁₂ O	l	787,000
Methyl-diethyl carbinol	C ₅ H ₁₄ O	l	927,000

*Acids**Final Products: CO₂(g), H₂O(l).*

Formic.....	CH ₂ O ₂	62,800
Oxalic.....	C ₂ H ₂ O ₄	60,150
Acetic.....	C ₂ H ₄ O ₂	208,000
Acetic anhydride..	C ₄ H ₆ O ₃	431,900
Glycolic.....	C ₂ H ₄ O ₃	166,600
Propionic.....	C ₃ H ₆ O ₂	365,000
Lactic.....	C ₃ H ₆ O ₃	326,000
d-tartaric.....	C ₄ H ₆ O ₆	275,100
n-butyric.....	C ₄ H ₈ O ₂	520,000
Citric (anhydrous).	C ₆ H ₈ O ₇	474,500
Benzoic.....	C ₇ H ₆ O ₂	771,840
o-phthalic.....	C ₈ H ₆ O ₄	771,000
Phthalic anhydride	C ₈ H ₄ O ₃	781,500
o-toluic.....	C ₈ H ₈ O ₂	928,900
Palmitic.....	C ₁₆ H ₃₂ O	2,380,000
Stearic.....		2,629,000
Elaidic.....		2,664,000
Oleic.....	C ₁₈ H ₃₄ O ₂	2,659,000
Stearic.....	C ₁₈ H ₃₆ O ₂	2,698,000

*Carbohydrates — Cellulose — Starch, etc.**Final Products: CO₂(g), H₂O(l).*

d-glucose (dextrose)..	C ₆ H ₁₂ O ₆	673,000
l-fructose.....	C ₆ H ₁₂ O ₆	675,000
Lactose (anhydrous).	C ₁₂ H ₂₂ O ₁₁	1,350,800
Sucrose.....	C ₁₂ H ₂₂ O ₁₁	1,349,600

*Calories
per gram*

Starch.....	4,179
Dextrin.....	4,110
Cellulose.....	4,181
Cellulose acetate.	4,496

TABLE XI. — *Continued**Other CHO Compounds**Final Products:* CO₂(g), H₂O(l).

Compound	Formula	State	Heat of Combustion
Formaldehyde.	CH ₂ O	<i>g</i>	134,000
Acetaldehyde..	C ₂ H ₄ O	<i>g</i>	280,000
Acetone.....	C ₃ H ₆ O	<i>l</i>	427,000
Methyl acetate	C ₃ H ₆ O ₂	<i>g</i>	397,700
Ethyl acetate..	C ₄ H ₈ O ₂	<i>g</i>	544,400
Ethyl acetate..	C ₄ H ₈ O ₂	<i>l</i>	538,500
Diethyl ether..	C ₄ H ₁₀ O	<i>l</i>	651,700
Diethyl ketone.	C ₅ H ₁₀ O	<i>l</i>	736,000
Phenol.....	C ₆ H ₆ O	<i>s</i>	732,000
Pyrogallol.....	C ₆ H ₃ O ₃	<i>s</i>	639,000
Amyl acetate..	C ₇ H ₁₄ O ₂	<i>l</i>	1,040,000
Camphor.....	C ₁₀ H ₁₆ O	<i>s</i>	1,411,000

*Nitrogen Compounds**Final Products:* CO₂, N₂(g), H₂O(l).

Urea.....	CH ₄ N ₂ O	<i>s</i>	152,000
Cyanogen.....	C ₂ N ₂	<i>g</i>	260,000
Trimethylamine.....	C ₃ H ₉ N	<i>l</i>	578,600
Pyridine.....	C ₅ H ₅ N	<i>l</i>	660,000
(1, 3, 5) Trinitrobenzene...	C ₆ H ₃ N ₃ O ₆	<i>s</i>	664,000
(2, 4, 6) Trinitrophenol.....	C ₆ H ₃ N ₃ O ₇	<i>s</i>	620,000
<i>o</i> -dinitrobenzene.....	C ₆ H ₄ N ₂ O ₄	<i>s</i>	703,200
Nitrobenzene.....	C ₆ H ₅ NO ₂	<i>l</i>	739,000
<i>o</i> -Nitrophenol.....	C ₆ H ₅ NO ₂	<i>s</i>	689,000
<i>o</i> -Nitroaniline.....	C ₆ H ₄ N ₂ O ₂	<i>s</i>	766,000
Aniline.....	C ₆ H ₇ N	<i>l</i>	812,000
(2, 4, 6) Trinitrotoluene...	C ₇ H ₅ N ₃ O ₆	<i>s</i>	821,000
Nicotine.....	C ₁₀ H ₁₄ N ₂	<i>l</i>	1,428,000

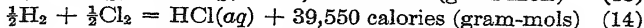
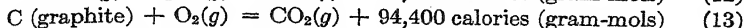
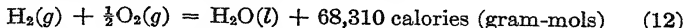
*Halogen Compounds**Final Products:* H₂O(l), dil. sol. of HCl.

Carbon tetrachloride.	CCl ₄	<i>g</i>	90,080
Carbon tetrachloride.	CCl ₄	<i>l</i>	82,180
Chloroform	CHCl ₃	<i>g</i>	96,250
Chloroform.....	CHCl ₃	<i>l</i>	89,200
Methyl chloride.....	CH ₃ Cl	<i>l</i>	164,000
Chloroacetic acid.....	C ₂ H ₃ ClO ₂	<i>s</i>	171,000
Ethylene chloride....	C ₂ H ₄ Cl ₂	<i>g</i>	271,000
Ethyl chloride.....	C ₂ H ₅ Cl ₂	<i>g</i>	321,800

*Sulphur Compounds**Final Products:* CO₂, SO₂(g), H₂O(l).

Carbonyl sulphide.	COS	<i>g</i>	130,500
Carbon disulphide.	CS ₂	<i>l</i>	246,600
Methyl mercaptan.	CH ₃ S	<i>g</i>	297,600
Dimethyl sulphide.	C ₂ H ₆ S	<i>g</i>	455,600
Ethyl mercaptan..	C ₂ H ₅ S	<i>g</i>	452,000

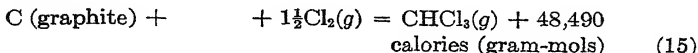
necessary to know the heats of formation of CO_2 , $\text{H}_2\text{O}(l)$, and $\text{HCl}(aq)$. These values may be obtained from Table X.



Solving (12), (13), and (14) for $\text{H}_2\text{O}(l)$, $\text{CO}_2(g)$, and $\text{HCl}(aq)$, respectively, and substituting in (11),

$$\begin{array}{rcl} + \frac{1}{2}\text{O}_2(g) + \text{I} & + \frac{1}{2}\text{O}_2(g) - 68,310 = \text{C (graphite)} & \\ - 94,400 &) - 118,650 + 96,250 & \end{array}$$

or,



In this manner a general equation may be derived for use in calculating the heat of formation of any compound of the formula $\text{C}_x\text{H}_y\text{Br}_z\text{Cl}_d$, $\text{F}_e\text{I}_f\text{N}_g\text{O}_h\text{S}_i$, from its heat of combustion. If Q_c is the heat of combustion corresponding to final products of $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$, $\text{Br}(l)$, $\text{Cl}_2(g)$, $\text{HF}(aq)$, $\text{I}(s)$, $\text{N}_2(g)$, $\text{SO}_2(g)$.

$$Q_F = -Q_c + 94,400a + 34,155b + 41,475e + 69,400i \quad (16)$$

If Q_c' is the heat of combustion corresponding to final products of $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$, $\text{Br}_2(g)$, $\text{HCl}(aq)$, $\text{HF}(aq)$, $\text{I}(s)$, $\text{HNO}_3(aq)$, $\text{H}_2\text{SO}_4(aq)$,

$$\begin{aligned} Q_F = -Q_c' + 94,400a + 34,155b - 7,650c + 5,395d + 41,475e \\ + 15,725g + 141,940i \end{aligned} \quad (17)$$

The coefficient of c in Equation (17) is the heat of formation of bromine vapor from liquid bromine, which is taken as the basis for the heats of formation of bromine compounds.

If neither Equation (16) nor (17) is applicable, the heat of formation of any compound may be calculated from its heat of combustion by the method demonstrated above in the algebraic combination of Equations (11), (12), (13), and (14).

When no data are available for the heat of combustion of a compound it is possible to calculate this information by means of a method proposed by Kharasch and Sher.^{1,2} These investigators have made a critical compilation² of all experimental data on heats of combustion. From this they have developed a method by which the heat of combustion of any compound may be calculated if its structural formula is known. The results calculated by this method rarely deviate from the better

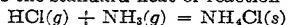
¹ J. Phys. Chem. **29**, 625-658 (1925).

² Bureau of Standards Journal of Research **2**, 359-430 (1929).

experimental values by more than 1 per cent, and in many cases the calculated are probably more reliable than the experimental values. The methods of calculation and the necessary data and corrections are thoroughly discussed in the two papers cited.

Calculation of the Standard Heat of Reaction. The standard heat of reaction accompanying any chemical change may be calculated if either the heats of formation or the standard heats of combustion of all compounds entering into the reaction are known. The reactants and products of a chemical reaction each represent a definite heat content relative to some arbitrary reference state. If the reference state for each compound is taken as the separate elements at 18° C and 1 atmosphere pressure in their normal state of aggregation then the relative heat content of each compound is equal to the negative value of its heat of formation. By means of a heat balance the standard heat of reaction may then be calculated by substituting for the symbols of a chemical equation the relative heat contents of the separate materials indicated. The standard heat of reaction from such a heat balance is equal to the relative heat content of the reactants minus the relative heat content of the products at standard conditions. The general rule in calculating the standard heat of reaction, Q_{18} , is to substitute for the symbol of each material in a chemical equation the negative value of its heat of formation, adding the value Q_{18} to the right-hand side of the equation to complete the heat balance. When an element enters into a reaction, its heat of formation is zero if it is in the form selected as the basis for the heat of formation data.

Illustration 1. Calculate the standard heat of reaction of the following:



From Table X the relative heat contents may be found directly

$$\text{HCl}(g)\Delta H = -Q_F = -22,050 \text{ calories per gram-mol}$$

$$\text{NH}_3(g)\Delta H = -Q_F = -10,940 \text{ calories per gram-mol}$$

$$\text{NH}_4\text{Cl}(s)\Delta H = -Q_F = -75,100 \text{ calories per gram-mol}$$

Substituting these values into a heat balance for the above reaction

$$-22,050 - 10,940 = -75,100 + Q_{18}$$

or

$$Q_{18} = 42,110 \text{ calories (gram-mol)}$$

The same result may be reached by considering that a chemical reaction is equivalent to the following series of processes:

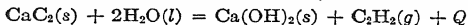
a. The reactants are decomposed into their elements, *absorbing* energy equal to the sum of the heats of formation of the reactants.

b. The elements formed in process a are recombined to form the final products of the reaction, evolving energy equal to the sum of the heats of formation of the final products.

The net heat of reaction is, then, the difference between the sum of the heats of formation of the products and the sum of the heats of formation of the reactants.

If an endothermic compound, whose heat of formation is negative, enters into a reaction, the heat of reaction may be calculated by either of the above methods, recognizing the negative value of the heat of formation.

Illustration 2. Calculate the standard heat of reaction, Q , of the following:



From Table X,

$$\begin{aligned}\text{CaC}_2(s) : Q_F &= 14,580 \text{ calories per gram-mol} \\ \text{H}_2\text{O}(l) : Q_F &= 68,310 \text{ calories per gram-mol} \\ \text{Ca}(\text{OH})_2(s) : Q_F &= 236,000 \text{ calories per gram-mol}\end{aligned}$$

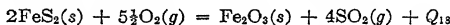
The heat of formation of acetylene may be calculated from the heat of combustion data of Table XI by means of Equation (17),

$$\text{C}_2\text{H}_2(g) : Q_F = -54,890 \text{ calories per gram-mol}$$

Substituting the negative values of the heats of formation into the reaction equation:

$$\begin{aligned}-14,580 - 136,620 &= -236,000 - (-54,890) + Q \\ Q &= 29,910 \text{ calories (gram-mols)}\end{aligned}$$

Illustration 3. Calculate the standard heat of reaction of the following:



The heats of formation, Q_F , of the compounds are obtained from Table X,

$$\begin{aligned}\text{FeS}_2(s) : Q_F &= 35,600 \text{ calories per gram-mol} \\ \text{Fe}_2\text{O}_3(s) : Q_F &= 191,600 \text{ calories per gram-mol} \\ \text{SO}_2(g) : Q_F &= 69,400 \text{ calories per gram-mol}\end{aligned}$$

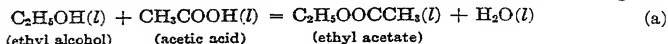
From the above rule,

$$\begin{aligned}-2 \times 35,600 + 5\frac{1}{2} \times 0 &= -191,600 - 4 \times 69,400 + Q_{18} \\ Q_{18} &= 398,000 \text{ calories (gram-mols)}\end{aligned}$$

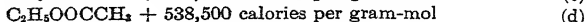
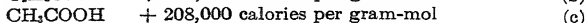
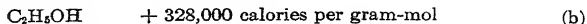
From Heat of Combustion Data. For a reaction between organic compounds the basic thermochemical data are generally available in the form of standard heats of combustion. The standard heat of reaction where organic compounds are involved can be conveniently handled by using directly the standard heats of combustion instead of heats of formation. A heat balance will again be employed, but in this case the standard reference state will not be the elements but the products of combustion at 18° C and 1 atmosphere pressure and in the state of aggregation as specified by the heat of combustion data. For example, the heat content of methane relative to its products of combustion, gaseous CO_2 and liquid H_2O , is equal to its standard heat of combustion, +212,790 calories per gram-mol. Therefore, in any equation involving combustible materials the formula of a compound may be replaced by its heat content relative to its products of combustion; the relative heat

content of the reactants minus the relative heat content of the products is equal to the standard heat of reaction, or the standard heat of combustion of the reactants minus the standard heat of combustion of the products is equal to the standard heat of reaction.

Illustration 4. Calculate the standard heat of reaction, Q_{1s} , of the following:



From Table XI heats of combustion are as follows:



Establishing a heat balance from the above equation,

$$+328,000 + 208,000 = 538,500 + 0 + Q$$

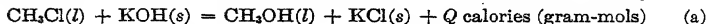
or

$$Q = -2500 \text{ calories (gram-mol)}$$

In general, the heats of formation of organic compounds are small in comparison to the heats of combustion from which they are determined. Similarly, the heats of reaction are small in systems involving only combinations of organic compounds. Since these relatively small quantities can be determined only by the differences between the large heats of combustion it follows that they are rarely known with a high degree of accuracy. For example, the small heat of reaction which is the final result of Illustration 4 is of very uncertain accuracy. An error of only 0.2 per cent in determining the heat of combustion of ethyl acetate would result in an error of 40 per cent in the value of this heat of reaction.

When both organic and inorganic compounds appear in a reaction it is best to obtain the heat of reaction by means of heat of formation data. The heats of formation of the organic compounds may be calculated from their heats of combustion by means of Equation (16) or (17). The procedure is then the same as that demonstrated in Illustration 2.

Illustration 5. Calculate the standard heat of reaction (Q) of the following:



The heats of formation, Q_F , of the inorganic compounds are obtained from Table X.

$$\text{KOH}(s) : Q_F = +102,000$$

$$\text{KCl}(s) : Q_F = +104,300$$

The heats of combustion, Q_c , of the organic compounds are obtained from Table XI, and the heats of formation, Q_F , calculated by means of Equation (17).

$$\text{CH}_3\text{Cl}(l) : Q_c = 164,000 \text{ calories per gram-mol}$$

$$Q_F = -164,000 + 94,400 + (3 \times 34,155) + 5395 = +38,260 \text{ calories per gram-mol}$$

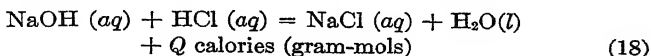
$$\text{CH}_3\text{OH}(l) : Q_c = 170,900 \text{ calories per gram-mol}$$

$$Q_F = -170,900 + 94,400 + (4 \times 34,155) = 60,120 \text{ calories per gram-mol}$$

Substituting the negative values of the heats of formation into (a):

$$\begin{aligned}-38,290 - 102,000 &= -60,120 - 104,300 + Q \\ Q &= +24,130 \text{ calories (gram-mols)}\end{aligned}$$

Heats of Neutralization of Acids and Bases. The neutralization of a dilute aqueous solution of NaOH with a dilute solution of HCl may be represented by the following thermochemical equation:

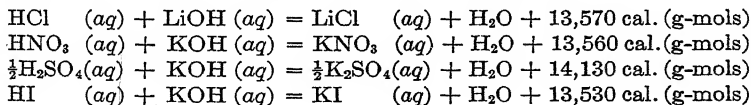


The heat of reaction, Q , may be calculated from the respective heats of formation, Q_F , in Table X. Thus,

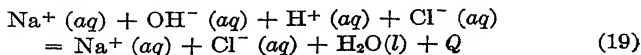
$$\begin{aligned}\text{NaOH (aq)}, Q_F &= 112,020 \text{ calories per gram-mol} \\ \text{HCl (aq)}, Q_F &= 39,550 \text{ calories per gram-mol} \\ \text{NaCl (aq)}, Q_F &= 97,020 \text{ calories per gram-mol} \\ \text{H}_2\text{O}, Q_F &= 68,310 \text{ calories per gram-mol}\end{aligned}$$

$$\begin{aligned}\text{Then } Q &= -112,020 - 39,550 + 97,020 + 68,310 \\ &= 13,760 \text{ calories (gram-mols)}\end{aligned}$$

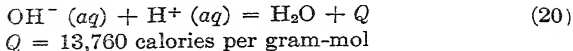
Heats of neutralization may be determined by direct calorimetric measurements in series of solutions of finite concentrations and these results extrapolated to correspond to infinite dilution. Following are heats of neutralization based, at least in part, on such measurements.



It will be noted that the heat of neutralization of strong acids with strong bases in dilute solution is practically constant when 1 mol of water is formed in the reaction. The explanation of this fact is that strong acids and bases and their salts are completely dissociated into their respective ions when in dilute aqueous solution. From this viewpoint, a dilute solution of hydrochloric acid consists of only hydrogen and chlorine ions in aqueous solution, and a dilute solution of sodium hydroxide consists of sodium and hydroxyl ions. Upon neutralization the resulting solution contains only sodium and chlorine ions. The reaction may be looked upon as ionic, and Equation (18) rewritten in ionic form.



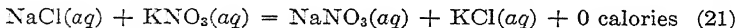
Canceling the similar terms from Equation (19),



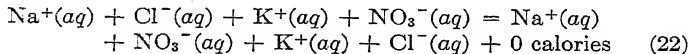
Thus, the actual net result of the neutralization of dilute solutions of strong acids and bases is the production of water from hydrogen and hydroxyl ions. The accepted average value of the heat of neutralization is 13,850 calories per gram-mol of water formed. This corresponds to the heat of reaction, Q , of Equation (20), representing the formation of water from its ions.

In the neutralization of dilute solutions of weak acids and weak base, the heat of neutralization is much less than 13,850 calories. For example, in the neutralization of hydrocyanic acid with sodium hydroxide, the heat evolved is only 2900 calories per gram-mol of water formed. The unevolved heat may be considered as the heat required to complete the dissociation of hydrogen cyanide into hydrogen and cyanide ions as neutralization proceeds. As a hydrogen ion from hydrogen cyanide is neutralized by a hydroxyl ion, more hydrogen cyanide ionizes until neutralization is complete. This ionization of hydrogen cyanide requires the absorption of heat at the expense of the heat evolved in the union of hydrogen and hydroxyl ions.

Thermoneutrality of Salt Solutions. When dilute aqueous solutions of two neutral salts are mixed there is no thermal effect provided there is no precipitation, or evolution of gas. However, upon evaporation of a mixture of such solutions four crystalline salts will be found, indicating that double decomposition or metathesis has taken place. For example,



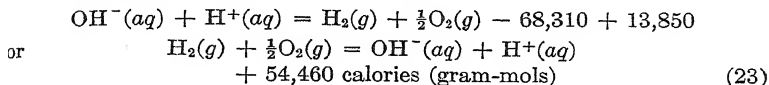
In dilute aqueous solutions it may be considered that each of these four salts is completely ionized and Equation (21) written in ionic form,



From this viewpoint it is evident that mixing such systems actually produces no change, the initial and final solutions consisting of the same four ions. It is only upon concentration of the solution and reassociation of the ions that the metathesis leads to a definite change in the nature of the system.

The experimentally observed fact that dilute solutions of neutral salts of strong acids and bases may be mixed without thermal effect is termed the *thermoneutrality of salt solutions*.

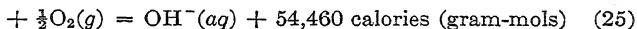
Heats of Formation of Ions. Equation (20) represents the formation of a mol of water from the combination of hydrogen and hydroxyl ions. The average value of this heat of reaction has been determined as 13,850 calories per gram-mol. The heat of formation of water from gaseous oxygen and hydrogen is given in Table X as 68,310 calories per gram-mol. Substituting these data in Equation (20),



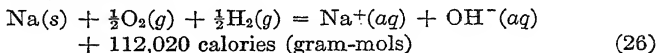
If the heat of formation from the normal elements of either ion of Equation (23) were known, the heat of formation of the other ion could be calculated. In order to establish values of the *relative* heats of formation of ions, that of the hydrogen ion has been arbitrarily assigned a value of zero. Thus, by definition,



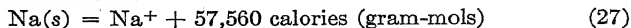
Combining (24) and (23), the relative heat of formation of the hydroxyl ion is obtained,



On this basis the relative heats of formation of the other ions of highly dissociated acids and bases may be calculated. For example, from Table X, the heat of formation of $\text{NaOH}(aq)$ is 112,020 calories per gram-mol. Since sodium hydroxide is completely dissociated into sodium and hydroxyl ions when in dilute solution, the formation of 1 mol of $\text{NaOH}(aq)$ from the elements is, in actual effect, the formation of 1 mol of sodium and 1 mol of hydroxyl ions. Thus,



Combining (26) and (25),



Therefore, the heat of formation of the sodium ion is 57,560 calories per gram-mol. In a similar manner the heats of formation of other ions may be calculated, based on the assignment of a value of zero to hydrogen. Heats of formation of a few common ions, calculated from the data of the International Critical Tables, are given in Table XII.

The heat of formation in dilute aqueous solution of any compound which is completely dissociated under these conditions is equal to the sum of the heats of formation of its ions. From the data of Table XII the heats of formation of such compounds may be predicted.

TABLE XII

HEATS OF FORMATION OF IONS

Data from the International Critical Tables

 Q_F = heat of formation, calories per gram-mol

$$Q_F = -\Delta H_F$$

Cations			Anions		
Ion	Formula	$Q_F = -\Delta H_F$	Ion	Formula	
Aluminum.....	Al ⁺⁺⁺	126,400	Acetate.....	CH ₃ COO ⁻	117,500
Ammonium.....	NH ₄ ⁺	43,100	Bicarbonate.....	3	164,500
Barium.....	Ba ⁺⁺	128,300	Bisulphate.....	HSO ₄ ⁻	209,500
Calcium.....	Ca ⁺⁺	129,500	Bisulphite.....	HSO ₃ ⁻	147,400
Hydrogen.....	H ⁺	0	Bromide.....	Br ⁻	28,600
Iron.....	Fe ⁺⁺	20,800	Carbonate.....	CO ₃ ⁻⁻	161,000
Iron.....	Fe ⁺⁺⁺	9,500	Chloride.....	Cl ⁻	39,550
Lithium.....	Li ⁺	66,500	Fluoride.....	F ⁻	78,300
Magnesium.....	Mg ⁺⁺	110,200	Hydroxide ..	OH ⁻	54,460
Manganese.....	Mn ⁺⁺	49,700	Iodide.....	I ⁻	13,300
Manganese.....	Mn ⁺⁺⁺	23,100	Nitrite.....	NO ₂ ⁻	25,580
Potassium.....	K ⁺	60,400	Nitrate.....	NO ₃ ⁻	49,800
Sodium.....	Na ⁺	57,560	Phosphate.....	PO ₄ ⁻⁻⁻	298,500
Zinc.....	Zn ⁺⁺	36,550	Sulphate.....	SO ₄ ⁻⁻	211,500
			Sulphite.....	SO ₃ ⁻⁻	146,700

Illustration 6. Calculate, from the data of Table XII, the heat of formation of barium chloride in dilute solution.

Since BaCl₂ may be assumed to be completely dissociated in dilute solution its heat of formation in dilute solution is equal to the sum of the heats of formation of one barium ion and two chlorine ions. From Table XII,

$$\text{Ba}^{++} : Q_F = 128,300 \text{ calories per gram-mol}$$

$$\text{Cl}^- : Q_F = 39,550 \text{ calories per gram-mol}$$

$$\text{BaCl}_2(aq) : Q_F = 128,300 + (2 \times 39,550) = 207,400 \text{ calories per gram-mol}$$

The heat of formation of a substance which is soluble and highly ionized in water may be calculated from its heat of formation in dilute solution from the heat of formation of its ions provided its standard heat of solution is known. Since experimental determinations of the heats of solution are relatively easy, a simple method is provided for estimating the heat of formation of many inorganic compounds. The heat of formation in infinitely dilute solution is calculated from the ionic heats of formation and the heat of solution subtracted from this value. For example, the standard heat of solution of BaCl₂(s) in an infinite amount of water is +2200 calories per gram-mol. From the result of Illustration 6, the heat of formation of BaCl₂(s) is 207,400 - 2200 or 205,200 calories per gram-mol.

Chemical reactions which take place between strong acids and bases and their salts in dilute aqueous solution may be treated as ionic and

heats of reaction calculated directly from ionic heats of formation. This method is particularly desirable when dealing with analytical data on complex solutions. By treating the reactions as ionic it is unnecessary to formulate hypothetical combinations of the analytically determined ionic quantities.

Heats of Gaseous Dissociation. At high temperatures the elementary gases are known to dissociate into their atomic states with absorption of great amounts of heat. Upon cooling, these monatomic gases rapidly recombine to form the original elementary gas. From an industrial standpoint, the most interesting phenomenon of this type is the dissociation of normal gaseous hydrogen, $H_2(g)$, to form a monatomic gas, $H(g)$. Such molecular dissociations in the gaseous state are accompanied by large absorptions of energy or negative heats of reaction. Conversely, the reassociation of the dissociated products is accompanied by a large evolution of energy. The rapid rate of association of atomic gases accompanied by a great evolution of heat is made use of in the recently developed atomic hydrogen welding process. Normal hydrogen is caused to dissociate into the atomic form. This active gas is brought into contact with the metallic surface to be heated, where it reassociates with the evolution of a large quantity of heat which is concentrated in a small volume and produces an extremely high temperature.

The heats of dissociation of a number of gases have been determined by various indirect methods. Many of these data are of questionable accuracy and are subject to frequent revision. The value for the dissociation of hydrogen is probably known with the greatest accuracy. In Table XIII are recently established data for the heats of reaction of several gaseous dissociations.

TABLE

$$Q = -\Delta H$$

= O(g)	— 63,000	calories (gram-mols)
= H(g)	— 50,500	calories (gram-mols)
= N(g)	— 105,000	calories (gram-mols)
= Cl(g)	— 28,800	calories (gram-mols)
= I(g)	— 10,400	calories (gram-mols)

HEAT OF SOLUTION

The heat of reaction accompanying the dissolution of a substance is termed its *heat of solution*, or better, its *heat of dissolution*. If chemical combination takes place between the solvent and the substance being dissolved, the heat of dissolution will include the *heat of solvation* or the

heat of hydration accompanying this combination. If ionization takes place the heat of solution will also include the energy of ionization. The heat of dissolution accompanying the formation of a solution from a unit quantity of pure solute and the quantity of *pure* solvent necessary to produce a specified concentration is termed the *integral* heat of dissolution of the solute at the specified concentration. If the solution is formed at 18° C from components at 18° C the thermal effect is termed the *standard* heat of solution. The integral heat of solution of a substance in pure solvent must be distinguished from the *differential* heat of solution, which is the heat of reaction accompanying the dissolution of a unit quantity of the substance in a relatively very large quantity of its *solution*. This latter property will be discussed in detail in the following section. When no specific designation is made, the term *heat of solution* implies the integral rather than the differential value.

The heat of solution of a neutral, non-dissociating salt which does not form a solvate is generally negative, corresponding to the absorption of heat in the formation of the solution. The dissolution of such a material is analogous to the evaporation of a liquid in that the ultimate result of each process is the breaking down of a condensed form of structure into a state of dispersion of its component units. In each process energy is absorbed in overcoming the attractive forces between the structural units of the condensed state. Heats of solvation, especially in aqueous systems, are generally positive and relatively large. For this reason, the heat of solution of a substance which forms a solvate or hydrate is generally positive and large, corresponding to the evolution of heat in the formation of the solution.

The standard heat of solution of a substance is dependent on the concentration of the solution formed. The effect of concentration on the heat of solution is diminished as the concentration is diminished. Thus, for dilute solutions the heat of solution is practically independent of concentration, and change of concentration is accompanied by no thermal effect. In dealing with aqueous solutions it generally may be assumed that heat of solution is independent of concentration in solutions containing more than 100 mols of water per mol of solute.

Integral Heats of Solution. In Figs. 26, 27, 28, 29, and 30, are graphically presented data on the standard integral heats of solution of common acids, bases, and salts in water. These data were calculated from the International Critical Tables. Integral heats of solutions are generally determined by calorimetrically measuring the heat of solution of a unit quantity of solute in enough solvent to form a relatively concentrated solution. The *heat of dilution* accompanying the addition of solvent to this concentrated solution is then measured. The heat of

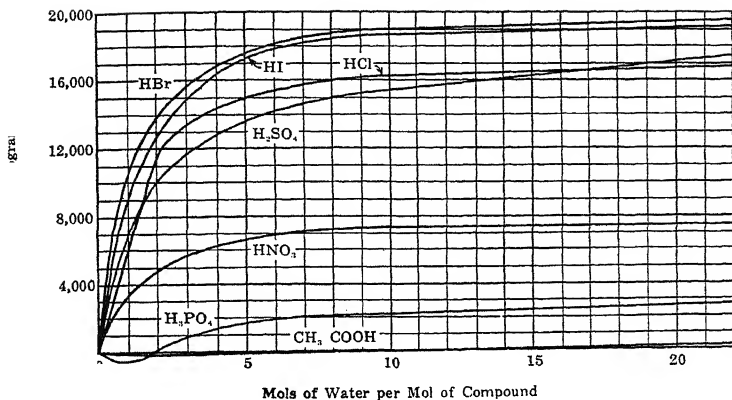


FIG. 26. Integral Heats of Solution of Acids in Water at 18° C.

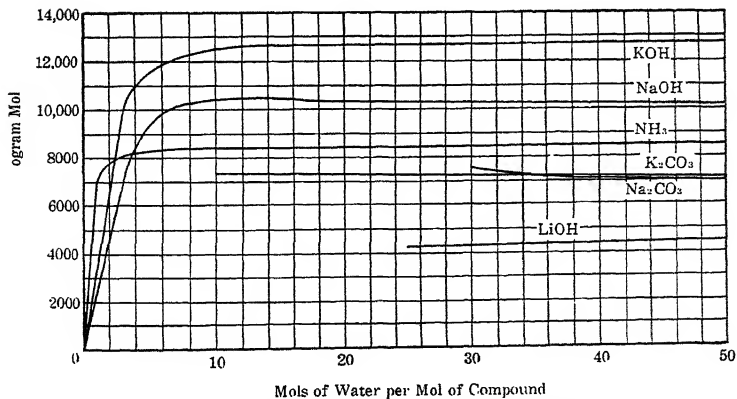


FIG. 27. Integral Heats of Solution of Alkalies in Water at 18° C.

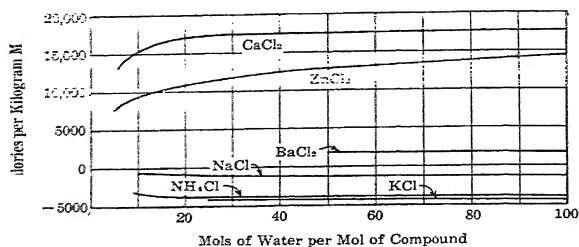


FIG. 28. Integral Heats of Solution of Chlorides in Water at 18° C.

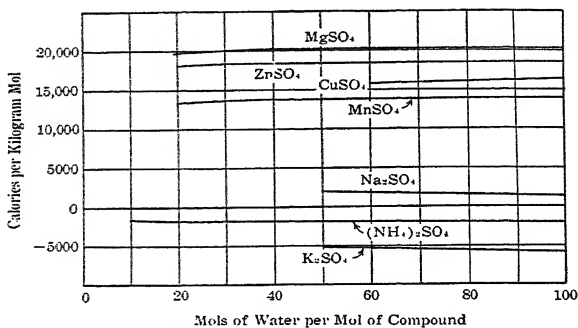
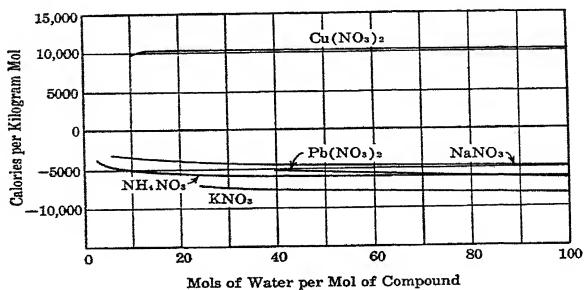


FIG. 29. Integral Heats of Solution of Sulphates in Water at 18° C.



30. Integral Heats of Solution of Nitrates in Water at 18° C.

solution at any desired concentration is obtained by adding together the observed heats of solution and dilution. Conversely, from the curves of Figs. 26 to 30, the heat of dilution accompanying a change in concentration may be calculated by subtracting the heat of solution at the initial concentration from that at the final concentration.

By combination of the data of Table X with those of Figs. 26 to 30 it is possible to calculate the heat of formation of a compound in an aqueous solution of specified concentration. This total heat of formation will be the sum of the heat of formation, Q_F , of the undissolved material and its standard integral heat of solution, Q_s , at the specified concentration.

Illustration 7. *a.* Calculate the heat of formation of H_2SO_4 to form an aqueous solution containing 5.0 mols of water per mol of H_2SO_4 .

b. Calculate the heat of dilution, per mol of solute, of the solution of part *a* to a concentration of 1 mol of H_2SO_4 per 20 mols of water.

Solution: *a.* From Table X:

$$\text{H}_2\text{SO}_4(l); Q_F = 189,750 \text{ calories per gram-mol}$$

From Fig. 26:

$$\text{H}_2\text{SO}_4(n_1 = 5.0); Q_s = 13,600 \text{ calories per gram-mol}$$

Therefore,

$$\text{H}_2\text{SO}_4(n_1 = 5.0); Q_F = 189,750 + 13,600 = 203,350 \text{ calories per gram-mol}$$

b. From Fig. 26:

$$\text{H}_2\text{SO}_4(n_1 = 20); Q_s = 17,200 \text{ calories per gram-mol}$$

Therefore,

$$\text{H}_2\text{SO}_4(n_1 = 5) + 15\text{H}_2\text{O} = \text{H}_2\text{SO}_4(n_1 = 20) + 3600 \text{ calories (gram-mols)}$$

If a solute forms a hydrate, the standard heat of solution of the hydrate is the difference between the heat of solution of the anhydrous substance and the heat of hydration. The heat of hydration may be calculated from the data of Table X as the difference between the heat of formation of the hydrated compound and the sum of the heats of formation of the anhydrous substance and of the water of hydration.

Illustration 8. Calculate the standard heat of solution of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to form a solution containing 10 mols of water per mol of CaCl_2 .

Solution: From Table X:

$$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}; Q_F = 623,500$$

$$\text{CaCl}_2; Q_F = 190,500$$

$$\text{H}_2\text{O}; Q_F = 68,310$$

Then,

$$\begin{aligned} \text{CaCl}_2 + 6\text{H}_2\text{O} &= \text{CaCl}_2 \cdot 6\text{H}_2\text{O} + Q_H \\ Q_H &= 623,500 - 190,500 - (6 \times 68,310) = 23,140 \text{ calories (gram-mols)} \\ &= \text{heat of hydration} \end{aligned}$$

From Fig. 28,

$$\text{CaCl}_2(n_1 = 10); Q_s = 15,500 \text{ calories per gram-mol}$$

Therefore,

$$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(n_1 = 4); Q_s = 15,500 - 23,140 = -7640 \text{ calories per gram-mol}$$

In dealing with integral heat of solution data, either component of a solution of finite concentration may be considered as the solute. For example, the heat of solution of 1 mol of CaCl_2 in 10 mols of water is 15,500 calories per gram-mol. Conversely, the molal heat of solution of 1 mol of water in $\frac{1}{10}$ mol of CaCl_2 is 1550 calories. From either viewpoint the heat of reaction accompanying the formation of a solution from 1 mol of CaCl_2 and 10 mols of water is equal to 15,500 calories.

The heat of solution data of systems in which both solute and solvent are liquids are frequently termed *heats of mixing*. Heats of mixing are generally expressed on the basis of a unit quantity of the solution formed. If 10 grams of glycerin are mixed with 90 grams of water the heat evolved is 191 calories. Therefore, the heat of mixing of water and glycerin to form a solution containing 10 per cent glycerin is 1.91 calories per gram of solution formed. The integral heat of solution of either component may be calculated from heat of mixing data.

Illustration 9. The heat of mixing of water and glycerin to form a solution containing 40% glycerin is 4.50 calories per gram of solution. Calculate the integral heats of solution of glycerin and of water at this concentration.

Basis: 100 grams of solution.

Heat of mixing = 450 calories.

$$\text{Heat of solution of glycerin in water} : \frac{450}{40} = 11.25 \text{ calories per gram.}$$

$$\text{Heat of solution of water in glycerin} : \frac{450}{60} = 7.5 \text{ calories per gram.}$$

Partial Heats of Solution. The gain in the total heat content of a binary solution per unit weight of solute when a relatively very small quantity of the pure solute is added to a fixed weight of solution at constant temperature is called the partial heat content of the solute and is expressed mathematically as

$$\bar{H}_2 = \left(\frac{\delta H}{\delta n_2} \right) \quad (28)$$

where \bar{H}_2 is the partial heat content of the solute per unit weight of solute

H is the total heat content of the solution containing weights w_1 of solvent and w_2 of solute

Similarly, the partial heat content of the solvent is the gain in heat content of the solution per unit weight of solvent when a relatively very small quantity of pure solvent is added to a fixed weight of solution.

The total heat content is the sum of the partial heat contents of the separate components as demonstrated in Chapter V, page 120. Thus,

$$H = w_1 \bar{H}_1 + w_2 \bar{H}_2$$

If ΔH is the gain in heat content of the system when w_2 units of solute are dissolved in w_1 units of solvent at constant temperature, and $\Delta \bar{H}_1$ and $\Delta \bar{H}_2$ are the gains in the partial heat contents of the solvent and solute respectively, when dissolved, then

$$\Delta H = w_1 \Delta \bar{H}_1 + w_2 \Delta \bar{H}_2 \quad (30)$$

or

$$\frac{\Delta H}{w_2} = \frac{w_1}{w_2} \Delta \bar{H}_1 + \Delta \bar{H}_2 = \Delta H_s \quad (31)$$

The loss in heat content of the system at constant temperature is the integral heat of solution and the loss in the partial heat content of either component when dissolved in the solution is termed the partial heat of solution of the corresponding component, that is,

$$Q_s = -\Delta H_s, \quad Q_1 = -\Delta H_1, \quad \text{and} \quad \bar{Q}_2 = -\Delta \bar{H}_2 \quad (32)$$

where \bar{Q}_1 , \bar{Q}_2 are the partial heats of solution of the solvent and solute, respectively.

Substituting these values in Equation (31):

$$Q_s = \frac{w_1}{w_2} \bar{Q}_1 + \bar{Q}_2 \quad (33)$$

The above equations may be used for molal quantities as well as for weight quantities.

Because of the parallel significance of gain in partial heat contents and partial heat capacities the same methods may be employed for calculating the former as were used in calculating partial heat capacities in Chapter V, page 120. If the gain in heat content of a solution, per unit weight of solvent, is plotted against the weight of solute present, the slope of a tangent to this curve represents the gain in partial heat content of the solute at a concentration corresponding to the point of tangency. Similarly, the method of tangent intercepts may be used by plotting the total relative heat content of the solution, per unit quantity

of solution, against the fraction of solute in the solution. The intercepts of a tangent to this curve with the ordinates corresponding to the pure components represent the gain in heat contents of the solute and solvent, respectively, at the concentration corresponding to the point of tangency. If the gain in partial heat content of one component of a binary solution is known, that of the other may be calculated from Equation (30) or (33).

For finite concentrations the partial and integral heats of solution are usually widely different, the integral heat of solution representing the heat evolved when one unit weight of a solute is dissolved in sufficient solvent to produce the given concentration, whereas the partial heat of solution represents the heat evolved, per unit weight of solute, when a very small amount is added to the solution of given concentration. The partial and integral heats of solution of a substance are numerically equal only for solutions of infinite dilution.

Since the partial heat of solution is equal numerically to the negative value of the gain in partial heat content per unit weight of component, and the integral heat of solution is equal to the negative value of the gain in heat content, it is evident that partial heats of solution can be obtained from the integral heats of solution in the same manner as partial heat contents are obtained from gain in total heat contents.

If the integral heat of solution per unit weight of solvent is plotted against the weight of solute present, the slope of a tangent to this curve represents the partial heat of solution at a concentration corresponding to the point of tangency. Similarly the method of tangent intercepts may be used by plotting the integral heat of solution, per unit weight of solution, against the fraction of solute in the solution. The intercepts of a tangent to this curve with the ordinates corresponding to the pure components represent the partial heats of solution of the solute and solvent, respectively, at the concentration corresponding to the point of tangency. Similarly if the partial heat of solution of one component is known, that of the other may be calculated from Equation (33).

Illustration 10. From the following data for the heats evolved when water and glycerin are mixed to form 1 gram of solution, calculate the partial heats of solution of water in glycerin and of glycerin in water, per gram of each component, at each of the designated concentrations. Plot curves relating the partial heats of solution of glycerin and of water to percentage of glycerin by weight.

Solution: Method of Tangent Slope. The values of w' , the grams of glycerin per 1000 grams of water, in the above table are calculated from the percentage composition of the solution. Thus, for a 40% solution of glycerin

$$w' = \frac{40}{60} \times 1000 =$$

Percentage Glycerin by Weight	Q	w'	Q'	w''	Q''	\bar{Q}_{s1}	\bar{Q}_{s2}
10	1.91	111	2120	0.6	13.5
20	3.21	250	4020	1.4	10.5
30	3.90	429	5560	2.1	8.4
40	4.50	668	7500	3.4	6.2
50	4.50	1000	9000	1000	9000	5.6	3.4
60	4.21	668	7000	6.5	2.65
70	3.70	429	5290	8.3	1.7
80	2.61	250	3260	11.4	0.8
90	1.79	111	1990	14.0	0.4

Q = heat of mixing, calories per gram of solution.

w' = grams of glycerin per 1000 grams of water.

w'' = grams of water per 1000 grams of glycerin.

Q' = integral heat of solution per 1000 grams of water.

Q'' = integral heat of solution per 1000 grams of glycerin.

\bar{Q}_{s1} = partial heat of solution of water, calories per gram.

\bar{Q}_{s2} = partial heat of solution of glycerin, calories per gram.

The values of Q' , the integral heat of solution per 1000 grams of water, are obtained by multiplying the heat of solution, per gram of solution, by the number of grams of solution ($w' + 1000$) which contains 1000 grams of water. For a 40% solution of glycerin

$$Q' = (668 + 1000) (4.50) = 7500 \text{ calories}$$

Values of w' are plotted as abscissas and values of Q' as ordinates in Fig. 31. The slope of a tangent to this curve is the partial heat of solution per gram, of glycerin \bar{Q}_{s1} in a solution of concentration corresponding to the abscissa of the point of tangency. For a 40% solution:

$$\text{Slope of tangent} = \frac{9600 - 3400}{1000} = 6.2$$

Therefore, \bar{Q}_{s1} , the partial heat of solution of 1 gram of glycerin in a solution containing 40% glycerin is equal to +6.2 calories per gram.

The corresponding values of \bar{Q}_{s2} , the partial heat of solution of water, are calculated from Equation (33). For a 40% solution:

Basis: 100 grams of solution.

$w_1 = 40$ grams

$w_2 = 60$ grams

$$\frac{100Q}{w_2} - \frac{w_1}{w_2} = \frac{+450 - (40)(6.2)}{60} = +3.4$$

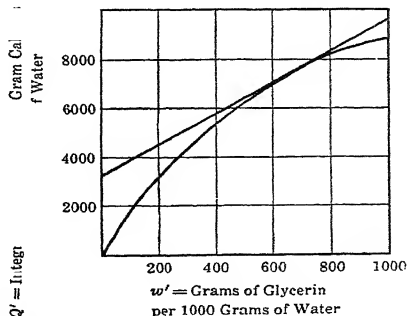


FIG. 31. Calculation of Partial Heats of Solution by the Tangent Slope Method.

It will be noted that at the higher concentrations of glycerin the slope of the curve of Fig. 31 becomes small and it is difficult to determine a value of \bar{Q}_{s1} from it with accuracy. For this reason it is inadvisable to use this curve in the range of concentrations above 50% glycerin. In this range more accurate graphical results may be obtained by plotting integral heats of solution for solutions containing 1000 grams of glycerin against the weight of water dissolved. From this curve values of \bar{Q}_{s2} are determined directly. The corresponding values of \bar{Q}_{s1} are calculated from Equation (33). In Fig. 32 values of w'' , the grams of water per 1000 grams of glycerin, are plotted as abscissas against Q'' , the integral heat of solution per 1000 grams of glycerin. The slope of a tangent to this curve is the partial heat of solution per gram of water in a solution

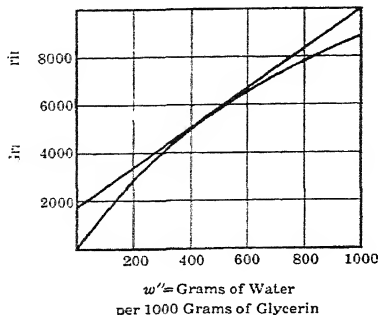


Fig. 32. Calculation of Partial Heats of Solution by the Tangent Slope Method.

of concentration corresponding to the abscissa at the point of tangency. For a 70% solution:

$$\begin{aligned} \text{Slope of tangent} \\ = \bar{Q}_{s2} &= \frac{10,000 - 1700}{1000} = 8.3 \text{ calories} \end{aligned}$$

From Equation (33), on the basis of 100 grams of solution:

$$\begin{aligned} \bar{Q}_1 &= \frac{100Q - w_2\bar{Q}_{s2}}{70} \\ &= \frac{+370 - (+8.3 \times 30)}{70} = +1.7 \end{aligned}$$

Solution: Method of Tangent Intercepts. Values of \bar{Q}_{s1} and \bar{Q}_{s2} may also be determined by plotting a curve relating the concentration of the solution, in weight percentages, to its integral heat of solution per gram of solution. In Fig. 33, curve I, are plotted the integral heats of solution for glycerin solutions, in calories per gram of solution, against weight percentages of glycerin. According to the development presented in Chapter V, page 125, the intercepts of a tangent to this curve with the ordinates of the pure components represent the partial heats of solution of the components. For example, line AB is tangent to curve I at the point corresponding to 40% glycerin by weight. The intercept,

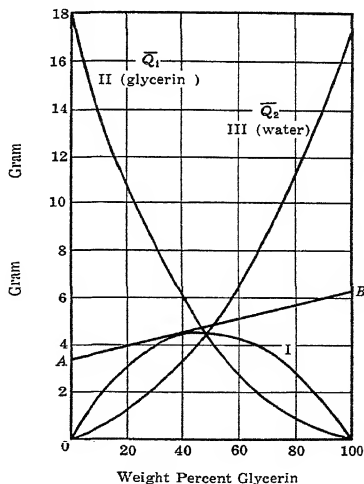


Fig. 33. ' Curve I: Calculation of Partial Heats of Solution by the Tangent Intercept Method. Curves II and III: Partial Heats of Solution of Glycerin and Water.

B , of this line with the axis representing 100% glycerin is $+6.2$, the value of \bar{Q}_{s1} at this concentration. Similarly, the intercept, A , at the axis representing 100% water is $+3.4$, the value of \bar{Q}_{s2} at this concentration. In a similar manner values of \bar{Q}_{s1} and \bar{Q}_{s2} at other concentrations may be determined.

The results of these calculations are summarized in the above table and presented graphically by curves II and III of Fig. 33. These curves express respectively the partial heats of solution, in calories per gram, of glycerin and of water at 18°C .

Heat Effects Accompanying Dissolution and Crystallization. *By Use of Integral Heats of Solution.* If additional solute is dissolved into a solution in such proportions that a large change in concentration results, the accompanying heat effect is most easily calculated from integral heat of solution data. Such a process is equivalent to the following series of processes:

a. The original solution is separated into pure solute and solvent, *absorbing* an amount of heat equal to the integral heat of solution of the solute present.

b. The original solute and that to be added are combined in the pure state and redissolved in the pure solvent, *evolving* an amount equal to the integral heat of solution of the total quantity of solute in the original quantity of solvent.

The net quantity of heat evolved is, then, the difference between the integral heat of solution of the total quantity of solute in the final solution and that of the solute in the original solution. Similar reasoning may be applied in calculating the heat evolved in mixing two solutions of different concentrations.

Illustration 11. An aqueous sulphuric acid solution contains 50% H_2SO_4 by weight. To 100 grams of this solution are added 75 grams of a solution containing 95% H_2SO_4 by weight. Calculate the quantity of heat evolved.

Solution:

Original Solution:

$\text{H}_2\text{SO}_4 = 50 \text{ grams or } 0.51 \text{ gram-mol}$

$\text{H}_2\text{O} = 50 \text{ grams or } 2.78 \text{ gram-mols}$

Mols H_2O per mol $\text{H}_2\text{SO}_4 = \frac{2.78}{0.51} = 5.45$

Heat of solution (Fig. 26) $= 13,800 \times 0.51 = 7050 \text{ calories}$

Solution Added:

$\text{H}_2\text{SO}_4 = 0.95 \times 75 = 71.2 \text{ grams or } 0.725 \text{ gram-mol}$

$\text{H}_2\text{O} = 0.05 \times 75 = 3.75 \text{ grams or } 0.208 \text{ gram-mol}$

Mols H_2O per mol $\text{H}_2\text{SO}_4 = \frac{3.75}{0.208} = 0.29$

Heat of solution $= 2000 \times 0.725 = 1450 \text{ calories}$

Final Solution:

$$\text{H}_2\text{SO}_4 = 0.725 + 0.51 = 1.235 \text{ gram-mols}$$

$$\text{H}_2\text{O} = 0.208 + 2.73 = 2.99 \text{ gram-mols}$$

$$\text{Mols H}_2\text{O per mol H}_2\text{SO}_4 = \frac{2.99}{1.235} = 2.42$$

$$\text{Heat of solution} = 10,800 \times 1.235 = 13,350 \text{ calories}$$

$$\text{Net heat evolved} = 13,350 - (7050 + 1450) = 4850 \text{ calories}$$

When solute is removed from a solution by a crystallization process, without change in the quantity of solvent, the accompanying heat effect may be calculated by the same type of reasoning. The heat *absorbed* in crystallization is the difference between the total heat of solution of the solute in the original solution and that of the solute in the final solution.

By Use of Partial Heats of Solution. If the concentration of a solution undergoes only a slight change in the addition or removal of one component, the resulting thermal effect may be calculated more accurately from partial heat of solution data than by the use of integral heats of solution shown in Illustration 11. The heat evolved in the dissolution of a unit quantity of solute into a solution is equal to the *average* partial heat of solution over the resultant concentration range. This average partial heat of solution may be calculated by graphically determining the average ordinate under a curve relating partial heats of solution, as ordinates, to concentrations expressed in quantities of solute per *unit quantity of solvent*. This procedure is equivalent to the integration of Equation (28) between the limits of the initial and final concentrations. Ordinarily, when dealing with small concentration changes, the average partial heat of solution may be assumed to be the arithmetic mean of the values corresponding to the initial and final concentrations.

Illustration 12. Calculate the heat evolved when 10 lb of water are added to 200 lb of an aqueous solution of glycerin containing 40% glycerin by weight.

Basis: 200 lb of original solution

$$\text{Glycerin} = 200 \times 0.40 = 80 \text{ lb}$$

$$\text{Final solution} = 200 + 10 = 210 \text{ lb}$$

Composition of final solution:

$$\text{Glycerin} = \frac{80}{210} = 38\%$$

$$\text{Water} = 62\%$$

From Fig. 33:

Differential heat of solution of water in glycerin:

$$\text{In initial solution} = 3.4 \text{ calories per gram}$$

$$\text{In final solution} = 3.2 \text{ calories per gram}$$

$$\text{Average} = 3.3 \text{ calories per gram or } 6.0 \text{ Btu per lb. Total heat evolved} = 6.0 \times 10 = 60 \text{ Btu.}$$

HEAT OF ADSORPTION

The adsorption of a gas or vapor by a solid (Chapter X, page 364) is accompanied by an evolution of heat of the same order of magnitude as that resulting from the normal condensation of the vapor to the liquid state. In general the heat of adsorption is considerably greater than that of normal condensation. Numerous theories have been advanced to explain this fact. There is evidence that an adsorbed gas exists in a highly compressed state, of greater density than in its normal liquid state. There is also evidence of loose chemical combination between the adsorbed gas and the adsorbent. On the basis of these observations it has been considered that the difference between the heats of adsorption and normal condensation represents energy of compression and chemical reaction.

Data on heats of adsorption are ordinarily presented either as integral or as differential values. The integral heat of adsorption is the heat evolved per unit weight of adsorbed gas when adsorbed on gas-free or "outgassed" adsorbent to form a definite concentration of adsorbate.

The integral heat of adsorption varies with the concentration of adsorbate, in general diminishing with an increase in concentration.

The differential or partial heat of adsorption of a gas is the heat evolved when a unit quantity of the gas is adsorbed by a relatively large quantity of adsorbent on which a definite concentration of the adsorbed gas already exists. The partial heat of adsorption is also a function of the concentration, in general diminishing with an increase in concentration. As complete saturation of an adsorbent is approached, the value of the partial heat of adsorption approaches that of the normal heat of condensation. In an adsorbent which does not possess submicroscopic capillaries and on which adsorption would be expected to be limited to formation of a monomolecular film, this change in heat of adsorption is very abrupt at the saturation-point. In such adsorbents the partial heat of adsorption shows relatively little change with increase in the quantity of adsorbed material until the surface is saturated. The heat of adsorption then drops abruptly to the heat of normal condensation. In an adsorbent possessing a high degree of submicroscopic capillarity, the change in heat of adsorption with change in concentration is more gradual, depending upon the number and size distribution of the capillaries.

It is apparent that integral and partial heats of adsorption bear the same relationship to each other as do integral and partial heats of solution. If, in the adsorption of a gram-mols of gas on a unit weight of

gas-free adsorbent, q calories are evolved, then

$$Q_A = \frac{q}{a} \quad (34)$$

$$\overline{Q}_A = \frac{\partial q}{\partial a} \quad (35)$$

where

Q_A = molal integral heat of adsorption

\overline{Q}_A = molal partial heat of adsorption

Values of partial heats of adsorption may be determined graphically by measuring the slope of a curve relating q and A . Partial heats of adsorption are convenient for industrial calculations because adsorbents are generally used in large masses in which concentration changes are small and gradual. When a large concentration change takes place in an adsorption process the thermal effect may be calculated by using the average partial heat of adsorption.

Experimental measurements have been made of the heats of adsorption of many of the more common gases on the important adsorbents such as charcoal, silica gel, and various solid catalysts. Consistent with other data on adsorption, these values are dependent to some extent on the physical state and method of treating the adsorbent material. If the previous history of the adsorbent is unknown some uncertainty will attend the application of published data to the adsorbent under consideration. However, although the previous history of the adsorbent has a pronounced effect upon the weight of gas adsorbed at saturation, it has a much smaller effect on the heats of adsorption. In Fig. 34 are values of partial heats of adsorption in calories per gram-mol adsorbed at 0° C, plotted against concentrations in cubic centimeters of adsorbed gas, measured at standard conditions of 0° C and 760 mm of mercury, per gram of adsorbent. Similar data for other systems may be found in the International Critical Tables (Vol. V, page 139), and the results of new measurements are continually appearing in the scientific literature. From such data the thermal effects accompanying industrial adsorption processes may be estimated.

Illustration 13. An adsorber for the removal of water vapor from air contains 250 lb of silica gel on which is initially adsorbed 28.0 lb of water. Calculate the heat evolved per pound of water adsorbed at this concentration, assuming that the characteristics of the gel are similar to that on which the data of Fig. 34 are based.

Solution: Concentration of H_2O in gel = $\frac{28}{250} = 0.112$ gram per gram SiO_2

or $\frac{0.112}{18} \times 22,400 = 139$ cc per gram of SiO_2

From Fig. 34 $\bar{Q}_A = 12,500$ calories per gram-mol
 or $12,500 \times 1.8 = 22,500$ Btu per lb-mol
 Heat evolved per pound of water adsorbed $= \frac{22,500}{18} = 1250$ Btu

Very few data are available concerning the effect of temperature on heats of adsorption. The Clapeyron equation (page 136) is applicable to the equilibrium between the gaseous and adsorbed phases of a gas or vapor and permits calculation of heats of adsorption from the slope of the

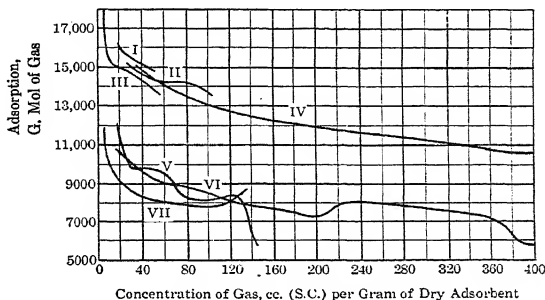


FIG. 34. Partial Heats of Adsorption.

- I. $\text{C}_2\text{H}_5\text{OH}$, 0°C on inactive coconut carbon, out-gassed at 350°C .
- II. C_6H_6 , 0°C on active coconut carbon, out-gassed at 350°C .
- III. $\text{C}_2\text{H}_5\text{OH}$, 0°C on active coconut carbon, out-gassed at 350°C .
- IV. H_2O , 0°C on silica gel dried at 300°C for 2 hr and out-gassed at 250°C , containing 3.5 — 5.5% H_2O .
- V. SO_2 , 0°C on same silica gel.
- VI. SO_2 , -10°C on blood carbon (puriss. Merck), out-gassed at 450°C ($d = 1.63$).
- VII. NH_3 , 0°C on coconut carbon, heated to 550°C , out-gassed at 400°C ($d = 1.86$).

adsorption isostere (page 364) relating temperature to the equilibrium pressure exerted by a constant concentration of adsorbed gas. This calculation is entirely analogous to the determination of heats of vaporization from vapor-pressure curves and is subject to the same limitations. Coolidge¹ finds good agreement between the results of this method and direct calorimetric determinations. On the basis of such calculated results he concludes that heats of adsorption at low concentrations show but little variation with change in temperature. In general, temperature appears to have little effect on the heats of adsorption of gases above their critical temperatures, especially where only monomolecular adsorp-

¹J. Am. Chem. Soc. **48** 1795 (1926).

tion would be expected. However, in the adsorption of vapors which are below the critical temperature, the heat of adsorption ordinarily approaches the value of the normal heat of condensation as the system approaches saturation. For this reason it would be expected that heats of adsorption corresponding to relatively high concentrations of such materials, particularly on capillary adsorbents, would diminish with increase in temperature, as do normal heats of condensation.

HEAT OF WETTING

When a dried solid surface is brought into contact with a liquid in which it is insoluble, a thin film of liquid will exist at the surface in an abnormal state similar to that of a film of adsorbed vapor. The liquid film may be highly compressed as a result of the attractive forces at the surface, and there may be combination of a chemical nature at the interface. The formation of such abnormal films of liquids is accompanied by a thermal effect, ordinarily an evolution of heat. The heat evolved when a solid surface is brought into contact with a liquid is termed the *heat of wetting*. Because of the very small amount of liquid affected by the interfacial forces of wetting, the heat of wetting per square centimeter of interfacial surface is a very small quantity. Heat of wetting is entirely negligible unless a very large area of interface is formed as in wetting a fine powder or a porous material. However, the thermal effects may then be of considerable importance, their magnitude depending upon the nature of both solid and liquid and on the area of interface formed.

Experimental measurements have been made of heats of wetting in many systems. Because of the uncertainty of the surface areas of materials whose heats of wetting are important, such data are ordinarily expressed in terms of the heat evolved when 1 gram of the solid is wetted with sufficient liquid so that further addition of liquid produces no thermal effect. This is termed the heat of *complete wetting*. Its magnitude is roughly proportional to the surface area exposed by a given weight of solid and is, of course, dependent on the quantity of the liquid originally present in the solid material. In Table XIV are experimental values of heats of wetting of dry clay, silica gel, starch, and charcoal by various liquids. The chemical and physical structures of the substances are not specified, and it must be recognized that these data may be used only for prediction of the order of magnitude of the effect to be expected in a specific case. Similar data for other systems are contained in the International Critical Tables (Vol. V, page 142). The heat of complete wetting of an adsorbent material by a liquid may be considered as the

difference between the integral heat of adsorption and the heat of normal condensation of a quantity of the vapor of the liquid sufficient to produce complete saturation of 1 gram of the adsorbent.

TABLE XIV

HEATS OF COMPLETE WETTING OF POWDERS DRIED AT 100° C

Experiments at 12° to 13° C.

Data from International Critical Tables, Vol. V, page 142.

Unit: calories per gram of the dry material.

Liquid	Clay	Amorphous Silica	Starch	Sugar Charcoal
H ₂ O (water).....	12.6	15.3	20.4	3.9
CH ₃ OH (methyl alcohol).....	11.0	15.3	5.6	11.5
C ₂ H ₅ OH (ethyl alcohol).....	10.8	14.7	4.9	6.8
C ₃ H ₁₁ OH (amyl alcohol).....	10.0	13.5	7.0	5.6
CH ₃ COOH (acetic acid).....	9.3	13.5	3.0-4.0	6.0
CH ₃ COCH ₃ (acetone).....	8.0	13.5	2.0	3.6
C ₂ H ₅ OC ₂ H ₅ (ether).....	5.8	8.4	2.2	1.2
C ₆ H ₆ (benzene).....	5.8	8.1	1.2	4.2
CCl ₄ (carbon tetrachloride)....	1.8	8.1	1.7	1.5
CS ₂ (carbon disulphide).....	1.7	3.6	0.5	4.0
C ₅ H ₁₂ , C ₆ H ₁₄ (pentane, hexane) .	1.2	3.1	0.3	0.4

As previously mentioned, the heat of wetting of a material is diminished if it originally contains even small traces of the liquid. This effect is shown graphically in Fig. 35 by plotting heats of complete wetting,

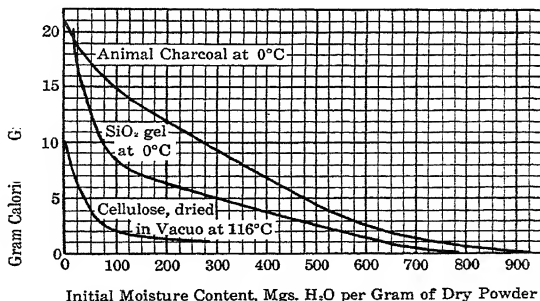


FIG. 35. Heats of Complete Wetting with Water.

per gram of dry material, against the milligrams of liquid originally present per gram of dry solid. The points at which the extrapolated curves approach the axis corresponding to zero heat of wetting indicate the minimum quantities of liquid required to produce complete wetting.

The heat evolved in the addition of liquid to a partially wetted solid is the difference between the heats of complete wetting at the final and the initial concentrations.

When a liquid is evaporated from a wetted adsorbent solid the heat required is greater than the normal heat of vaporization of the liquid removed by the amount of the heat of wetting of the dried material finally produced. This additional heat which must be supplied corresponds to the work which must be done in removing the adsorbed molecules away from the attractive forces holding them to the surface. However, the heat of wetting is ordinarily negligible in drying and cal-
cinating calculations.

Illustration 14. Wet silica gel contains 500 mg of H_2O per gram of dry SiO_2 . Estimate the number of Btu which must be supplied to dry 20 lb of this material at 20°C until it contains only 50 mg of H_2O per gram of dry SiO_2 .

20 lb of wet gel.

$$\text{Dry SiO}_2 \quad 20 \times \frac{1000}{1500} \quad 13.33 \text{ lb}$$

Heats of complete wetting (Fig. 35)

Final conditions = 13.4 calories/gram SiO_2

Initial condition = 2.6 calories/gram SiO_2

Heat evolved in wetting = $(13.4 - 2.6) \times 1.8 \times 13.33 = 260 \text{ Btu}$

Water removed in drying = $\left(\frac{500 - 50}{1000}\right) \times 13.33 = 6.0 \text{ lb}$

From Fig. 9:

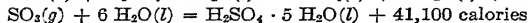
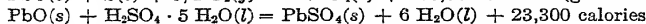
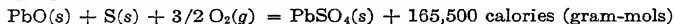
Heat of vaporization of water at 20°C (68°F) 18,930 Btu per lb-mol

Heat of vaporization = $\frac{6}{18.0} \times 18,930 = 6310 \text{ Btu}$

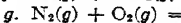
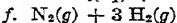
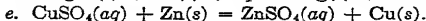
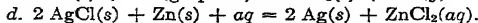
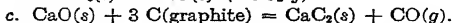
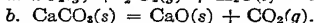
Total heat required = $6310 + 260 = 6570 \text{ Btu}$

PROBLEMS

1. Calculate the heat of formation, in calories per gram-mol, of $\text{SO}_3(g)$ from the following experimental data on standard heats of reaction.



2. From heat of formation data, calculate the standard heats of reaction of the following reactions, in Calories per kilogram-mol.



3. Calculate the heats of formation of the following compounds from the standard heat of combustion data. The combustion of CCl_4 is really hydrolysis.

- Benzene (C_6H_6)(*l*).
- Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$)(*l*).
- Oxalic acid ($(\text{COOH})_2$)(*s*).
- Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)(*l*).
- Carbon tetrachloride (CCl_4)(*l*).

4. Calculate the standard heats of reaction of the following reactions, expressed in calories per gram-mol.

- $(\text{COOH})_2(\text{s}) = \text{HCOOH}(\text{l}) + \text{CO}_2(\text{g})$.
(oxalic acid) (formic acid)
- $\text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{O}_2(\text{g}) = \text{CH}_3\text{COOH}(\text{l}) + \text{H}_2\text{O}(\text{l})$.
(ethyl alcohol) (acetic acid)
- $2 \text{CH}_3\text{Cl}(\text{g}) + \text{Zn}(\text{s}) = \text{C}_2\text{H}_6(\text{g}) + \text{ZnCl}_2(\text{s})$.
(methyl chloride) (ethane)
- $3 \text{C}_2\text{H}_2(\text{g}) = \text{C}_6\text{H}_6(\text{l})$.
(acetylene) (benzene)
- $(\text{CH}_3\text{COO})_2\text{Ca}(\text{s}) = \text{CH}_3\text{COCH}_3(\text{l}) + \text{CaCO}_3(\text{s})$.
(calcium acetate) (acetone)

5. The integral heat of solution of LiCl in water to form a solution of infinite dilution is +8440 calories per gram-mol. Calculate the heat of formation of $\text{LiCl}(\text{s})$ from the data of Table XII (page 178).

6. a. Calculate the number of Btu evolved at 18°C when 90 lb of ZnCl_2 are added to 150 lb of water.

b. Calculate the number of Btu evolved when 50 lb of CaCl_2 are added to 200 lb of an aqueous solution containing 10% CaCl_2 by weight at 18°C .

7. In the following table are values of the standard integral heats of solution, Q_s , in calories per gram-mol, of liquid acetic acid in water to form solutions containing m mols of water per mol of acid. (From International Critical Tables, Vol. V, page 159.)

m	Q_s
0.25	- 70
0.58	- 126
1.11	- 149
1.42	- 149
1.95	- 130
5.00	- 24
6.19	+ 13
30.00	+ 92
63.3	+ 107

- Using the method of tangent slope, calculate the partial molal heat of solution of acetic acid in a solution containing 15% acetic acid by weight.
- Using the method of tangent intercepts, calculate the differential molal heats of solution of acetic acid and of water in a solution containing 50% acetic acid by weight.

8. From the data of Problem 7 calculate the heat, in Btu, evolved when 10 lb of acetic acid are added to 1000 lb of a solution containing 50% acetic acid by weight. Perform the calculation both from integral heat of solution data and from differential heat of solution data derived in Problem 7.

9. From the integral heat of solution data of Problem 7 calculate the heat, in calories, which is evolved at 18° C when 1 liter of aqueous acetic acid containing 75% acid by weight is diluted to 2 liters by the addition of water.

10. The heats of mixing, in calories per gram-mol of solution, of carbon tetrachloride (CCl_4) and aniline ($\text{C}_6\text{H}_5\text{NH}_2$) at 25° C are given in the following table. (From the International Critical Tables, Vol. V, page 155.)

Mol fraction CCl_4	Q
0.0942	— 98
0.1848	— 169
0.3005	— 237
0.4152	— 282
0.4827	— 291
0.5504	— 293
0.6215	— 288
0.7175	— 270
0.7888	— 246
0.8627	— 188
0.9092	— 149

- Calculate the integral and partial molal heat of solution of each component in a solution containing 50% CCl_4 by weight.
- Calculate the heat evolved, in Btu, when 1 lb of aniline is added to a large quantity of solution containing 40% CCl_4 by weight.

11. Activated charcoal is used for the recovery of benzene (C_6H_6) vapors from a mixture of inert gases. Calculate the heat evolved, in Btu, per pound of benzene adsorbed on a large quantity of charcoal at 0° C, when the charcoal contains 0.25 lb of benzene per pound of charcoal.

12. Calculate the heat evolved, in Btu, when 1 lb of SO_2 gas is adsorbed on 6.0 lb of outgassed silica gel at 0° C.

13. Estimate the heat evolved, in Btu, in completely wetting 10 lb of dried clay with water.

14. Silica gel (amorphous silica) contains 12% H_2O by weight. Calculate the heat, in calories, evolved when 2.0 kg of this material at 0° C are completely wetted with water.

15. From the International Critical Tables obtain the following data:

- Heat of formation of $\text{SnBr}_4(c)$; calories per gram-mol.
- Heat of fusion of $\text{SnBr}_4(c)$; calories per gram-mol.
- Integral heat of solution of $\text{SnBr}_4(l)$ in a large amount of water; calories per gram-mol.
- Integral heat of solution of $\text{O}_2(g)$ in water to form a dilute solution; Btu per pound-mol.
- Integral heat of solution of 1.0 mol of $\text{HCl}(g)$ in 400 mols of water; Btu per pound-mol.
- Heat of transition of rhombic to monoclinic sulphur; calories per gram-mol.
- Standard heat of combustion of *o*-toluic acid ($\text{C}_8\text{H}_8\text{O}_2(s)$); calories per gram.
- Heat of mixing of $\text{CS}_2(l)$ and ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2(l)$); calories per gram-mol of mixture.

- i.* Total heat evolved in the adsorption of 65 cc of CO_2 on 1 gram of outgassed coconut charcoal at 0°C ; calories.
- j.* Differential heat of adsorption of CH_3OH vapors on activated charcoal containing 100 cc of vapor per gram of charcoal at 0°C ; calories per gram-mol.
- k.* Heat of wetting of dried bone charcoal with gasoline; calories per gram of charcoal.

CHAPTER VII

THERMOCHEMISTRY OF INDUSTRIAL REACTIONS AND FUELS

INCOMPLETE AND SUCCESSIVE REACTIONS

In the preceding chapter consideration was given to the thermal effects accompanying chemical reactions in which the reactants were present in stoichiometric proportions and the reactions went to completion. In industrial processes excess reactants are nearly always present and the reactions are seldom complete.

In a reaction proceeding at standard conditions the presence of unchanged reactants has no effect on the energy change per mol of reactant transformed. If an excess reactant passes through the process unchanged it possesses the same energy content at the end as at the beginning of the reaction. In calculating the heat evolved in uncompleted reactions at standard conditions, consideration is given only to the quantities which have reacted chemically. The standard heat of reaction is then calculated from the heats of formation or combustion of these quantities of reactants and products.

Frequently the chemical transformations of the same reactant proceed in successive steps or in divergent stages, and the quantities of different products which are formed bear no stoichiometric relationship to one another. For example, in the combustion of carbon, both carbon monoxide and carbon dioxide are formed in variable proportions which depend entirely upon the conditions of the reaction. In such reactions the standard heat of reaction may be calculated by exactly the same general procedure followed when all materials are present in stoichiometric proportions. The heats of formation of the quantities of reactants which actually react are merely subtracted from the heats of formation of the products actually formed. Or the heats of combustion of the products actually formed may be subtracted from the heats of combustion of the reactants transformed.

Illustration 1. In the production of metallic manganese, 10 kg of manganese oxide, Mn_2O_3 , are heated in an electric furnace with 3.0 kg of amorphous carbon (coke). The resulting products are found to contain 4.8 kg of manganese metal and 2.6 kg of manganous oxide, MnO , as slag. The remainder of the products consists of unconverted charge and carbon monoxide gas. Calculate the standard heat of reaction of this process for the entire furnace charge.

Solution:

Initial $\text{Mn}_2\text{O}_4 = 10.0 \text{ kg or } 10/229 =$	0.0437 kg-mol
Initial C = 3.0 kg or 3.0/12 =	0.250 kg-atom
Mn formed = 4.8 kg or 4.8/55 =	0.0874 kg-atom
MnO formed = 2.6 kg or 2.6/71 =	0.0366 kg-mol
Unconverted $\text{Mn}_2\text{O}_4 = 0.0437 - \frac{0.0874 + 0.0366}{3} =$	0.0024 kg-mol
O in final CO = $4(0.0437 - 0.0024) - 0.0366 =$	0.1286 kg-atom
CO formed =	0.1286 kg-mol
Unconverted C = $0.250 - 0.1286 =$	0.1214 kg-mol

Weight balance (verification)

Materials entering		Materials leaving	
Mn_2O_4	10.0 kg	Mn	4.8 kg
C	3.0 kg	MnO	2.6 kg
Total	13.0 kg	$\text{Mn}_2\text{O}_4 = 0.0024 \times 229 =$	0.55 kg
		CO = $0.1286 \times 28 =$	3.6 kg
		C = $0.1214 \times 12 =$	1.45 kg
			13.00 kg

Heats of formation of active reactants (data from Table X, page 159)

$\text{Mn}_2\text{O}_4 = 328,000(0.0437 - 0.0024) =$	13,600 Calories
C(coke) = $-2600(0.250 - 0.1214) =$	-335 Calories
Total	13,265 Calories

Heats of formation of products actually formed:

MnO = $90,800 \times 0.0366 =$	3,330 Calories
CO = $26,780 \times 0.1286 =$	3,440 Calories
Mn =	0 Calories
Total	6,770 Calories

Heat of reaction $Q = +6770 - 13,265 = -6495 \text{ kg. Calories.}$

EFFECT OF PRESSURE ON HEAT OF REACTION

In Chapter V it was pointed out that the total internal energy of an ideal gas is dependent only on its temperature and independent of its pressure. Therefore, in any system in which all gaseous components behave as ideal gases the total internal energy is independent of pressure, and since the product pV is independent of pressure the total heat content is likewise independent of pressure. Moreover, changes in pressure have negligible effects on the internal energy contents and heat contents of solids and liquids. If a reaction proceeds under constant conditions of temperature, the accompanying change in total internal energy is constant and independent of the pressure conditions, provided the gaseous components behave as perfect gases. Thus, if the same reaction is caused to proceed first under pressure conditions (1) and then under

different conditions of pressure (2), the temperature conditions being the same in both cases,

$$\Delta E_1 = \Delta E_2 \quad (1)$$

$\Delta E_1, \Delta E_2$ = increase in total internal energy under pressure conditions (1) and (2), respectively.

$$\text{Similarly,} \quad \Delta H_1 = \Delta H_2 \quad (2)$$

where $\Delta H_1, \Delta H_2$ = increase in total heat content under pressure conditions (1) and (2), respectively.

Therefore, *the heat of reaction at constant pressure is independent of the pressure provided that, in a reaction where gases are involved, these gases behave ideally, and provided when liquids or solids are present the changes in volume are negligible.* For incompressible systems this statement is exact.

Reactions at Constant Volume. From Equation (1) the decrease in internal energy accompanying a chemical reaction is the same whether it proceeds under conditions of constant pressure or under conditions of constant volume provided the gases present behave ideally. If the reaction proceeds in a calorimeter at 18° C at constant volume the heat evolved can be measured and is equal to the loss in internal energy.

$$= -\Delta E_v \quad (3)$$

If there is no change in the product pV during the reaction then the loss in heat content will also equal the heat evolved. If, however, the reaction proceeds with an increase in number of gaseous mols then there will be an increase in pV equal to $V \Delta p$ at constant volume. The total decrease in heat content can then be calculated from the relation:

$$\Delta H = \Delta E + V \Delta p \quad (4)$$

$$\text{or} \quad Q_v = -\Delta E \quad (5)$$

If Δn represents the increase in number of gaseous mols, then for ideal gas behavior

$$V \Delta p = \Delta n RT \quad (6)$$

$$\text{or} \quad Q_p = Q_v - \Delta n RT \quad (7)$$

The heat of reaction at constant pressure can be measured directly by allowing the reaction to proceed in a constant-pressure calorimeter at constant temperature. In this case the increase in pV will be $p \Delta V$. This external work of expansion under constant pressure and constant temperature will be extracted from the calorimeter, and the heat actually

measured, Q_p , will be less than Q_v by the heat equivalent of this external work, or

$$Q_p = Q_v - p \Delta V \quad (8)$$

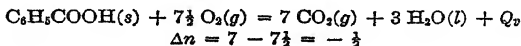
Since $p \Delta V$ is equal to ΔnRT ,

$$Q_p = Q_v - \Delta nRT \quad (9)$$

The heat of reaction at constant pressure is less than the heat of reaction at constant volume by the heat equivalent of the increase in the product pV or when there is an increase in number of gaseous mols by the heat equivalent of the product ΔnRT for ideal gas behavior.

The difference between heats of reaction at constant pressure and constant volume is of particular value in correcting experimental determinations of heats of reaction to constant pressure conditions. Calorimetric reactions are for the most part conducted at conditions of constant volume. Standard heats of reaction and formation are calculated from such data by means of Equation (9).

Illustration 2. In the combustion of 1 gram-mol of benzoic acid C_6H_5COOH at constant volume and a temperature $18^\circ C$, forming liquid water and gaseous CO_2 , 710,910 calories are evolved. Calculate the standard heat of combustion of benzoic acid.



From Equation (9)

$$Q_p = Q_v - \Delta nRT = 710,910 + (\frac{1}{2} \times 1.99 \times 291) = 711,200 \text{ calories (gram-mols)}$$

Reaction under High Pressures and Varying Pressures. At high pressures the total energy content and heat content of a substance are no longer independent of pressure due to variations in compressibility factors from unity. These conditions will be discussed in Chapter XIII.

The differences between heats of reaction at constant pressure and at constant volume and the effects of small changes of pressure during a reaction are generally small and frequently neglected. Since the majority of industrial reactions proceed under substantially constant pressures, detailed consideration will be given to the thermal effects accompanying only this type of reaction.

EFFECT OF TEMPERATURE ON HEAT OF REACTION

Standard heats of reaction represent the quantities of equivalent heat evolved during a reaction at constant pressure in which all reactants are initially at a selected standard temperature and all products are finally existent at that same temperature. Such conditions are rarely encountered in industrial reactions. Various reactants may enter at

different temperatures and the various products may each leave at still different temperatures. The heat effects of such reactions may be calculated from data on standard heats of reaction and thermophysical properties.

Since energy changes depend only on initial and final conditions, the heat of reaction corresponding to any non-standard temperature condition is equal to the algebraic sum of the thermal effects accompanying the following series of processes, if the gaseous components may be assumed to follow the simple gas law.

1. All materials entering the reaction are cooled or heated at constant pressure to form their standard states of aggregation at 18° C.
2. The reaction is allowed to proceed at 18° C.
3. All the resultant materials are heated or cooled at constant pressure to the respective temperatures and states of aggregation in which they leave the process.

If the reaction proceeds at a constant pressure, the thermal effect accompanying step 2 is the standard heat of reaction. Therefore, the heat of reaction at constant pressure corresponding to any condition of temperature is equal to the algebraic sum of the heat evolved in bringing all entering materials to their standard states of aggregation at a temperature of 18° C, plus the standard heat of reaction, minus the heat absorbed in bringing all resultant products to their respective final temperatures and states, all at the existing constant pressure. The heat evolved in changing the temperature of any material to produce the standard state of aggregation at 18° C is equal to the sum of both the sensible and the latent heat changes involved in the change.

Heat Balances. The heat evolved in bringing a reactant at constant pressure to its standard state of aggregation at 18° C is the total relative heat content of the original substance with respect to this standard condition. Similarly, the heat absorbed in changing a product at constant pressure from its standard state of aggregation at 18° C to any other condition is its total relative heat content in the final state, referred to the standard state at 18° C. Therefore, from the conclusion of the preceding paragraph,

$$H_R + Q_{18} = Q + H_P \quad (10)$$

where Q_{18} = standard heat of reaction

Q = heat evolved by the reaction under existing conditions

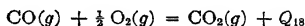
H_R = heat content of all reactants referred to their standard states of aggregation at 18° C and their existent pressures

H_P = heat content of all products, referred to their standard states of aggregation at 18° C and their existent pressures

The equality represented by Equation (10) is termed a *heat balance*. The left side of the equation represents what may be considered as the total relative heat input; the right side represents the corresponding heat output. The term Q represents all heat, radiant, and electrical energy lost by the system. Equation (10) and the concept of the heat balance are very useful in calculating and verifying the thermal changes accompanying relatively complex processes. The total heat content terms may be calculated from the data for the latent heats and heat capacities at constant pressure of each component.

Illustration 3. Carbon monoxide at 200° C is burned under atmospheric pressure with dry air at 500° C in 90% excess of that theoretically required. The products of combustion leave the reaction chamber at 1000° C. Calculate the heat evolved in the reaction chamber in Calories per kilogram-mol of CO burned, assuming complete combustion.

Basis: 1.0 kg-mol of CO.



From the data of Table XI, page 168

$Q_{18} =$	67,620 Calories (kg-mols)
O_2 required =	0.5 kg-mol
O_2 supplied = $0.5 \times 1.90 =$	0.95 kg-mol
Air supplied = $0.95/0.21 =$	4.52 kg-mols
N_2 present = $4.52 - 0.95 =$	3.57 kg-mols
Unused $\text{O}_2 = 0.95 - 0.50 =$	0.45 kg-mol

Relative heat content of reactants (H_R):

Carbon monoxide:

$$c_p(18-200^\circ \text{C}) = 6.99 \text{ Calories per kg-mol (Fig. 12, page 116)}$$

$$\text{Heat content} = 6.99 \times 1.0 \times (200 - 18) = 1270 \text{ Calories}$$

Air:

$$c_p(18 - 500^\circ \text{C}) = 7.1 \text{ Calories per kg-mol}$$

$$\text{Heat content} = 7.1 \times 4.52 \times (500 - 18) = 15,500 \text{ Calories}$$

$$\text{Total} = 15,500 + 1270 = 16,770 \text{ Calories} = H_R$$

Relative heat content of products (H_P):

Carbon dioxide:

$$c_p(18 - 1000^\circ \text{C}) = 11.2 \text{ Calories per kg-mol}$$

$$\text{Heat content} = 11.2 \times 1.0 \times (1000 - 18) = 11,000 \text{ Calories}$$

Oxygen and Nitrogen: $(3.57 + 0.45 = 4.02 \text{ kg-mols})$

$$c_p(18 - 1000^\circ \text{C}) = 7.32 \text{ Calories per kg-mol}$$

$$\text{Heat content} = 7.32 \times 4.02 \times (1000 - 18) = 28,900 \text{ Calories}$$

$$\text{Total} = 28,900 + 11,000 = 39,900 \text{ Calories}$$

From Equation (10):

$$\text{Heat evolved} = 16,770 + 67,620 - 39,900 = 44,490 \text{ Calories}$$

Heat balance:

	<i>Entering</i>		<i>Leaving</i>
Heat content of CO	1,270 Calories	Heat content of CO ₂	11,000 Calories
Heat content of air	15,500 Calories	Heat content of O ₂ and N ₂	28,900 Calories
Standard heat of reaction	67,620 Calories	Heat evolved	44,490 Calories
	84,390 Calories		84,390 Calories

Kirchhoff's Equation. A useful mathematical expression for the effect of temperature on heat of reaction may be derived for the special case of reactions which begin and terminate with all materials at the same temperature. Consider a reaction having a heat of reaction Q_T when carried out at a constant temperature T . If this reaction were carried out at a slightly higher constant temperature, $T + dT$, the heat of reaction would be $Q_T + dQ$. This heat of reaction is equal to the sum of the heat evolved in cooling all reactants at constant pressure to a temperature T , plus the heat of reaction at temperature T , minus the heat absorbed in heating all products to the temperature $T + dT$. Mathematically,

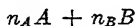
$$Q_T + dQ = C_p dT + Q_T - C_p' dT$$

$$\text{or} \quad dQ = -(C_p' - C_p) dT = -\Delta C_p dT \quad (11)$$

where C_p, C_p' = heat capacities at constant pressure of all reactants and products, respectively.

ΔC_p = increase in heat capacity of entire system at constant pressure resulting from the reaction.

Equation (11), known as Kirchhoff's equation, may be applied to any reaction, represented by the following general equation:



where

n_A, n_B , etc., = numbers of mols of components A, B , etc.

For this reaction:

$$- \cdot \cdot \cdot) \quad (12)$$

As pointed out in Chapter V, the variation with temperature of the molal heat capacity of a substance may usually be represented by a parabolic equation of the form:

where a_A, b_A , and c_A are constants, characteristic of the substance A . Each heat capacity term in Equation (12) may be replaced by such an

equation, the constants of which are empirically determined. Then,

$$\Delta C_p = \Delta a + \Delta b T + \Delta c T^2 + \dots \quad (13)$$

where

$$\Delta b = -$$

Substituting (13) in (11) and integrating:

$$Q = -\Delta a T - \frac{1}{2} \Delta b T^2 - \frac{1}{3} \Delta c T^3 - \dots + Q_0 = -\Delta H_T \quad (14)$$

The constant of integration, Q_0 of Equation (14), may be evaluated from knowledge of a single value of Q and its corresponding temperature. All other constants of the equation may be obtained directly from the heat capacity equations of the reactants and products.

Equation (14) is of great thermodynamic importance especially in determining the effect of temperature upon chemical equilibria. The utility of this equation and curves derived therefrom are limited to reactions which begin and end at the same temperature. To determine the energy changes and distributions in all industrial chemical processes the general method of solution by means of a heat balance is preferable and necessary.

HEATING VALUES OF FUELS

Most of the fuels used in industrial processes are of complex and uncertain chemical compositions. Direct experimental measurements are necessary in order to determine the thermal properties of such materials. The data ordinarily calculated are standard heats of complete combustion which are termed *heating values*.

Total and Net Heating Values. The major products of complete combustion from practically all fuels are carbon dioxide, water, and sulphur dioxide. Two methods of expressing heating value are in common use, differing in the state selected for the water present in the system after combustion. The *total heating value* of a fuel is the heat of reaction accompanying its complete combustion under constant pressure at a temperature of approximately 18° C when all the water formed and originally present as liquid in the fuel is condensed to the liquid state. The *net heating value* is similarly defined except that the final state of the water in the system after combustion is taken as vapor at 18° C. The total heating value is sometimes termed the "higher" or "gross" heating value; the net is often termed the "lower" heating value. The net heating value is obtained from the total heating value by subtracting the latent heat of vaporization at 18° C of the water formed and vaporized in the combustion.

When the heating value of coal is determined by burning coal in a calorimeter the sulphur is oxidized to form sulphuric acid. Normally the sulphur in coal burns to form sulphur dioxide only, so that a correction should be made to the calorimetric value for the heat evolved in forming sulphuric acid from sulphur dioxide and water.

Coke, Amorphous Carbon. The combustible constituents of cokes and charcoals are practically pure carbon. The heating value of such a fuel may be predicted with accuracy sufficient for many purposes by simply multiplying its carbon content by the heating value per unit weight of carbon.

In Table X of Chapter V, page 159, it will be noted that heats of formation of carbon compounds are based on a value of zero assigned to the heat of formation of β graphite. On this basis various other forms of elementary carbon have negative heats of formation. Several types of "amorphous" carbon are included in the table, each having a different heat of formation. These differences are believed to arise in part from differences in allotropic forms and in the surface energy of carbon in different states of subdivision and porosity, and in part from the presence of hydrocarbon compounds of high molecular weights and very low hydrogen contents.

The heats of combustion of the various forms of amorphous carbon differ by the same amounts as do their heats of formation. For combustion calculations the value of the heat of combustion of carbon is almost universally taken as 97,000 calories per gram-atom or 14,550 Btu per pound. This value is the difference between the heat of formation of carbon dioxide and that of carbon in coke, given in Table X page 159 or $97,000 = 94,400 - (-2600)$.

Coal Analyses. Coal consists chiefly of organic matter of vegetable origin which has been altered by decomposition, compression, and heating during long ages of inclusion in the earth's crust. In addition to organic matter it contains mineral constituents of the plants from which it was formed and also inclusions of other inorganic materials deposited in it during its geological formation.

Two types of analysis are in common use for expressing the composition of coal. In an *ultimate analysis*, determination is made of each of the major chemical elements. In a *proximate analysis* four arbitrarily defined groups of constituents are determined and termed *moisture*, *volatile matter*, *fixed carbon*, and *ash*. Following are the ultimate and proximate analyses of a typical Illinois coal:

<i>Ultimate</i>		<i>Proximate</i>	
Moisture.....	9.61	Moisture.....	9.61
Ash (corrected).....	9.19	Ash.....	9.37
Carbon.....	66.60	Volatile matter.....	30.68
Net hydrogen.....	3.25	Fixed carbon.....	50.34
Sulphur.....	0.49		
Nitrogen.....	1.42		100.00
Combined H ₂ O.....	9.44		
	100.00		

The proximate analysis of coal should be carried out according to an arbitrarily standardized procedure which has been recommended by the United States Bureau of Mines. The details of this method are described in any complete textbook on methods of technical analysis. The determinations may be very rapidly and easily carried out, and the majority of the contracts and specifications for the purchase of coal are based on this analysis. The tedious methods of ultimate analysis are completely carried out only when necessary to serve as a basis for heat and weight balance calculations. However, the sulphur content is of particular interest, and determination of this element frequently accompanies the proximate analysis.

In both schemes of analysis "moisture" represents the loss in weight on heating the finely divided coal at 105° C for one hour. The material termed "ash" in the proximate analysis is the residue from complete oxidation of the coal at a high temperature in air. This quantity is very useful as a basis for the calculation of the quantity of refuse formed in the ordinary combustion of the coal. However, the ash, determined in this manner, does not accurately represent the mineral content of the original coal because of the changes which take place during combustion. An important mineral component of many coals is iron pyrites, FeS₂. In combustion this is oxidized to form Fe₂O₃, which is weighed in the residual ash, and SO₂ gas. In the oxidation of pyrites 4 gram-atoms (128 grams) of sulphur are replaced by 3 gram-atoms (48 grams) of oxygen, a loss in weight equal to $\frac{2}{3}$ times the weight of pyritic sulphur present. Thus, in order to determine the actual mineral content of the coal, including the pyritic sulphur, it is necessary to add to the ash-as-weighed, a correction equal to $\frac{2}{3}$ of the pyritic sulphur content. To determine the actual mineral content, *not* including the pyritic sulphur, a correction equal to $\frac{3}{2}$ of the pyritic sulphur must be subtracted from the ash-as-weighed. Other less important corrections may also be applied to the ash. Unless otherwise designated, "ash" refers to ash-as-weighed.

To obtain the ultimate analysis, direct determinations are made of

carbon, sulphur, nitrogen, and hydrogen by the usual analytical methods. The moisture and ash are determined by the standardized procedures of the proximate analysis. The percentage oxygen content is then taken as the difference between 100 and the sum of the percentages of carbon, hydrogen, sulphur, nitrogen, and corrected sulphur-free ash. It is recommended that, for this calculation, the corrected ash be estimated by assuming that all sulphur in the coal is present in the pyritic form. On this basis,

$$\% \text{ corrected ash} = \% \text{ ash-as-weighed} - \frac{8}{3} \% \text{ S} = \\ \% \text{ mineral content} - \% \text{ S}$$

where $\% \text{ S}$ = percentage sulphur content of coal. This correction represents only an approximation, since not all sulphur is pyritic and other changes in the mineral constituents may take place in combustion. More refined methods for estimating oxygen content are not ordinarily justified.

In reporting the ultimate analysis it is convenient to consider that all oxygen is in combination with hydrogen to form moisture and "combined water." The surplus hydrogen, above that required to combine with the oxygen, is termed "net" or "available" hydrogen. This represents the hydrogen present in the form of hydrocarbons and available for further oxidation.

Rank of Coal. The sum of the fixed carbon and volatile matter of a coal is termed the *combustible*. The Bureau of Mines has published extensive tables¹ of the ultimate analyses of coals representing hundreds of coal deposits throughout the United States. If the source of a coal is known the ultimate analysis of its combustible matter can be obtained with fair reliability from these tables since the composition of combustible material in any one coal bed is nearly constant. In every coal sample it is necessary, however, to make separate determinations of ash and moisture content.

The *fuel ratio* of a coal is defined as the ratio of its percentage of fixed carbon to that of volatile matter. The *rank* of the coal, whether bituminous, or anthracite, may be estimated from the fuel ratio. The generally accepted classification of coals and the corresponding ranges of fuel ratios are as follows:

¹ U. S. Bureau of Mines, Bulletin 123

TABLE XV
RANK OF COALS

Rank	Fuel Ratio
Anthracite	between 10 and 60
Semi-anthracite	between 6 and 10
Semi-bituminous	between 3 and 7
Bituminous	between $\frac{1}{2}$ and 3

Fuels of lower rank than bituminous, namely, sub-bituminous and lignite, may have fuel ratios within the bituminous range but are characterized by higher water or oxygen contents.

The classification of coals on the basis of fuel ratio is not entirely satisfactory for many purposes. Several other methods¹ have been developed which give more nearly exact differentiation.

Heating Value of Coal. The total heating value of a coal may be determined by direct calorimetric measurement and is usually expressed in Btu per pound. The net heating value is obtained by subtracting from the total heating value the latent heat of vaporization at 18° C of the water present in the coal and that formed by the oxidation of the available hydrogen. Thus,

$$\text{Net } H.V. = \text{Total } H.V. - 9 \times H \times 1056 \quad (15)$$

where $H.V.$ = heating value, Btu per pound.

H = weight fraction of total hydrogen, including available hydrogen, hydrogen in moisture, and hydrogen in combined water.

Many attempts have been made to develop a method of calculating the heating value of coal from its proximate analysis. None of these methods are sufficiently reliable to justify their use except as rough approximations.

A fair approximation to the heating value of a coal may be obtained by considering that each of the combustible constituents, carbon, available hydrogen, and sulphur, is present in its elementary state. On the basis of this assumption the heating value is the sum of the quantities of heat evolved in the combustion of each of these elements, using for carbon the heating value of amorphous carbon and for sulphur the heating value of FeS_2 . The respective heats of combustion, in Btu per pound, may be obtained from the data of Table X, page 159. It is assumed that sulphur is burned to SO_2 .

¹ Haslam and Russell, "Fuels and Their Combustion," McGraw-Hill Book Co. (1926).

<i>Element</i>	<i>Heat of Combustion</i>
Carbon	14,550 Btu per pound
Hydrogen (total)	61,000 Btu per pound
Hydrogen (net)	51,550 Btu per pound
Sulphur (as FeS_2)	5,600 Btu per pound

Then,

$$\text{Total } H.V. = 14,550 C + 61,000 H_a + 5600 S \quad (16)$$

where

$H.V.$ = heating value, Btu per pound
 C, H_a, S = weight fractions of carbon, available hydrogen, and sulphur, respectively

Equation (16) is frequently termed Dulong's formula. It is not theoretically sound because it neglects the heats of formation of the compounds of carbon, sulphur, and hydrogen which actually exist in the coal. However, as previously pointed out, the heats of formation of hydrocarbon compounds are small in comparison to their heats of combustion, and the results of the above equation are rarely in error by more than 3 per cent. The experimentally observed total heating value of the coal whose analysis is given above, page 209, was 11,725 Btu per pound. Applying Equation (16), the heating value would be predicted as $(14,550 \times 0.666) + (61,000 \times 0.0325) + (5600 \times 0.0049) = 11,710$ Btu per pound, an error of -0.1 per cent.

Because of the fact that the heating value of coal is more easily determined than its ultimate analysis, the use of Equation (16) for calculation of heating value is rarely advantageous. It is more useful as a means of predicting the available hydrogen content from experimentally determined values of carbon and sulphur contents and heating value.

A useful relationship has been pointed out by Uehling¹ between the heating value of coal *per pound of total carbon* and its rank. It was found that, for each rank of coal, the heating value per pound of total carbon is practically constant, rarely varying by more than 2 per cent. It was also found that the weight of available hydrogen, per pound of total carbon, varies but little among coals of the same rank. On this basis, standard average heating values and available hydrogen contents, per pound of total carbon, were established for the different ranks of fuel. These values, contained in the following table, were based on the published results of a large number of analyses carried out by the United States Bureau of Mines.

¹E. A. Uehling, "Heat Loss Analysis," McGraw-Hill Book Co. (1929).

TABLE XVI

STANDARD HEATING VALUES AND NET HYDROGEN CONTENTS OF COAL

 $H.V.$ = heating value, Btu per pound of total carbon. H_a = available hydrogen content, pounds per pound of total carbon.

Rank	$H.V.$	H_a
Coke.....	14,550	0.0
Anthracite.....	16,100	0.029
Semi-bituminous.....	17,400	0.049
Bituminous.....	17,900	0.054
Sub-bituminous.....	17,600	0.045
Lignite.....	17,100	0.037

From the data of Table XVI, the heating value of the bituminous coal whose analysis was given on page 209 would be predicted as $17,900 \times 0.666 = 11,920$ Btu per pound, in error by only 1.7 per cent as compared to the experimentally determined value of 11,725. The available hydrogen content would be predicted as $0.666 \times 0.054 \times 100 = 3.6$ per cent as compared to the experimentally observed value of 3.25 per cent.

Because of the relative difficulty of the total carbon determination as compared to the calorimetric determination of heating value, the relationships pointed out by Uehling promise to be of greatest value in predicting the ultimate analysis from the experimentally determined heating value. From only the heating value and the data of Table XVI, good approximations to the total carbon and available hydrogen content of a coal may be predicted. In view of the fact that the composition of a coal sample will frequently vary by as much as 5 per cent from the true average composition of the coal from which it was taken, the accuracy of these predictions is often as great as is justifiable for calculations of heat and weight balances.

PETROLEUM

Petroleum oils are complex mixtures of hydrocarbons including four important series of compounds: paraffins, naphthenes, olefins, and aromatics. These compounds differ in hydrogen content in the order listed, paraffins having the highest hydrogen contents and aromatics the lowest. In naturally occurring petroleum the first two series predominate; in *cracked* products formed by decomposition of natural oils large quantities of olefins and aromatics may also be present. In addition to hydrocarbons varying quantities of sulphur, oxygen, and nitrogen compounds are generally present.

Because of the complexity of petroleum fractions determination of the actual compounds present is generally impossible. Elementary analyses

may be made, determining carbon, hydrogen, sulphur, and nitrogen as for coal. Data of this type are available for many naturally occurring petroleum in the publications of the U. S. Bureau of Mines. However, such analyses give little indication of the actual character of an oil and its thermal properties. However, methods have been developed whereby much of this information may be estimated from easily determined physical properties such as the distillation or boiling range, the specific gravity, and the viscosity.

Characterization of Petroleum. For general correlation of the average physical properties of petroleum stocks of different types, it is necessary to develop a means of quantitatively expressing the general character of the oil. Paraffin hydrocarbons of maximum hydrogen content may be considered as one extreme and aromatic materials of minimum hydrogen content as the other.

To serve as a quantitative index to this property, which may be termed paraffinicity, the U.O.P. characterization factor¹ has been developed and empirically related to six commonly available laboratory inspections. Although this factor is not an exact measure of chemical type and does not show perfect constancy in a homologous series, these disadvantages are, to a considerable extent, offset by its simplicity and convenience of definition and use.

The definition of the U.O.P. characterization factor arose from the observation that, when a crude oil of supposedly uniform character is fractionated into narrow cuts, the specific gravity of these cuts is approximately proportional to the cube roots of their absolute boiling-points. The proportionality factor may then be taken as indicative of the paraffinicity of the stock. Thus

(17)

where

$$\begin{aligned} K &= \text{U.O.P. characterization factor} \\ T_B &= \text{average boiling-point, degrees Rankine} \\ S &= \text{specific gravity at } 60^\circ \text{ F} \end{aligned}$$

When dealing with mixtures of wide boiling range a special method of obtaining the average boiling-point as described by Watson and Nelson must be used. For narrower cuts the 50 per cent point of the Engler distillation may be taken as the average boiling-point.

The characterization factor shows fair constancy throughout the boiling range of a number of crude oils and for others may either increase or decrease in the higher boiling range. In the paraffin series fair con-

¹ Watson, Nelson, and Murphy, *Ind. Eng. Chem.* **25**, 880 (1933); **27**, 1460 (1935).

stancy for the average of the reported isomers exists up to a boiling temperature of 700° F. Values of the characterization factor range as follows:

Pennsylvania stocks.....	12.2-12.5
Midcontinent stocks	11.8-12.0
Gulf Coast stocks.....	11.0-11.5
Cracked gasolines.....	11.5-11.8
Cracking plant combined feeds...	10.5-11.5
Recycle stocks.....	10.0-11.0
Cracked residuums.....	9.8-11.0

The characterization factor is readily calculated from Equation (17) from only the specific gravity and average boiling-point, or it may be read directly from A.P.I. gravity and average boiling-point by interpolation between the curves of Fig. 36. In this figure, A.P.I. gravities are plotted as ordinates and average boiling-points as abscissas with lines of constant K from Equation (17). The relationship between specific gravity and degrees A.P.I. is shown by Fig. 96 in the Appendix.

It has also been found that a fair empirical correlation exists between the characterization factor and the viscosity-gravity relationship at a given temperature. Paraffinic stocks have high viscosities as compared to aromatic materials of the same gravities.

Because of uncertainties of molecular aggregation at low temperatures, the viscosity measurements used for physical correlations should be made at as high temperature as possible. In Fig. 37 viscosity in centistokes at 122° F is plotted against A.P.I. gravity for stocks of constant characterization factors. By use of the centistoke scale of viscosity the entire range of fractions from light gasolines to heavy residues is covered in a single relationship. A table for conversion of common viscometer readings into centistokes is included in the Appendix, page 476.

Lines of constant boiling-point are plotted on Fig. 37 resulting from combination of the relationships between characterization factor from boiling-point and viscosity data. These lines permit an approximation to the boiling-point from only viscosity and gravity data. This relationship is particularly useful for heavy stocks on which boiling-point data can be obtained only under high vacuum. However, because of the large change in viscosity with a slight change in the gravity of heavy stocks, boiling-points estimated in this way may be considerably in error, sometimes as much as 50° F for the heavier residues. Similar charts were developed on the basis of viscosities at other temperatures.¹

Molecular Weights. The average molecular weights of petroleum fractions may be satisfactorily estimated from average boiling-point

¹ Watson, Nelson, and Murphy, *Ind. Eng. Chem.* **27**, 1460 (1935).

and gravity. Aromatic stocks of low characterization factors have lower molecular weights than paraffinic materials of the same average boiling-points.

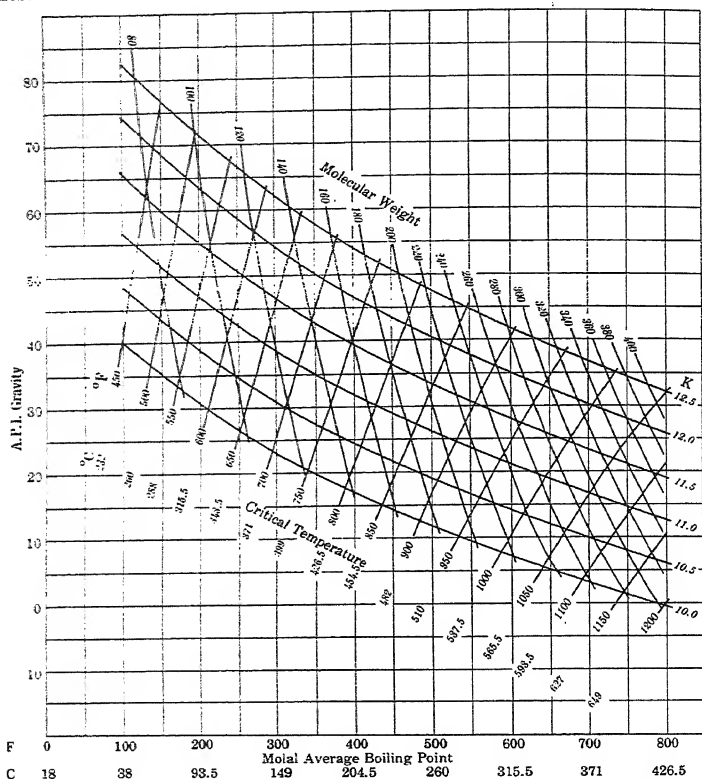


FIG. 36. Molecular Weights, Critical Temperatures and Characterization Factors of Petroleum Fractions.

The relationship between molecular weight, characterization factor, boiling-point, and A.P.I. gravity is included in the curves of Fig. 36. By interpolation between these curves, molecular weights may be estimated with errors rarely exceeding 5 per cent. If boiling-point data are not available, the boiling-point may be estimated from viscosity using Fig. 37.

Critical Properties. The critical temperature curves of Fig. 36 were calculated directly from Equation (5), Chapter IV, but are in satisfactory agreement with the existing data on petroleum.

Critical temperatures estimated from Fig. 36 are applicable with little error to pure hydrocarbons, narrow petroleum cuts, or wide-boiling mixtures if a proper method of obtaining average boiling-point is used.

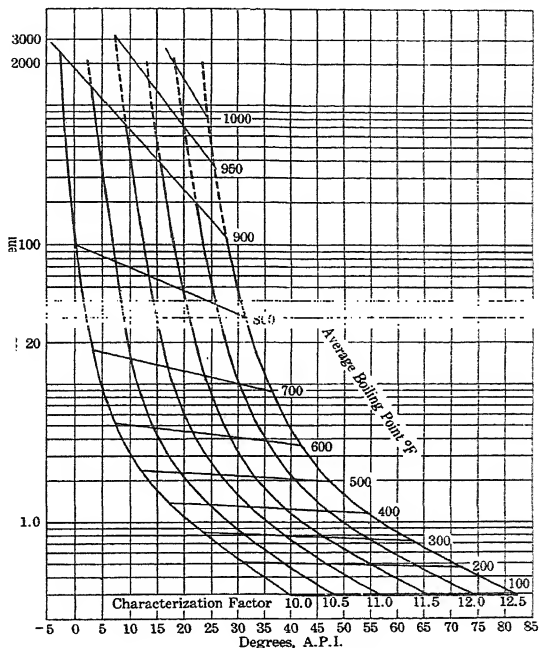


FIG. 37. Characterization Factor from Viscosity at 122° F.

The critical pressure of a pure compound is readily estimated by extrapolating its vapor pressure curve to the critical temperature and reading the corresponding pressure. The complete curve relating average boiling-point to pressure for a petroleum fraction may be estimated from its boiling-point by use of Fig. 4, page 73. The critical pressure is approximately the pressure on this curve at the critical temperature if the fraction has a narrow boiling range, for materials of wider boiling-range special methods must be used.

Hydrogen Content. The curves of Fig. 38 represent a relationship between hydrogen content and characterization factor for materials of constant boiling-points.

Figure 38 combined with the preceding charts permits estimation of hydrogen content from a knowledge of only the specific gravity and one other property. Ordinarily the error will be less than 0.5 per cent, based on the total weight of the oil, except for highly aromatic, low-boiling materials.

Petroleum oils ordinarily contain little ash and in the absence of specific data may be assumed to be 97 per cent carbon and hydrogen

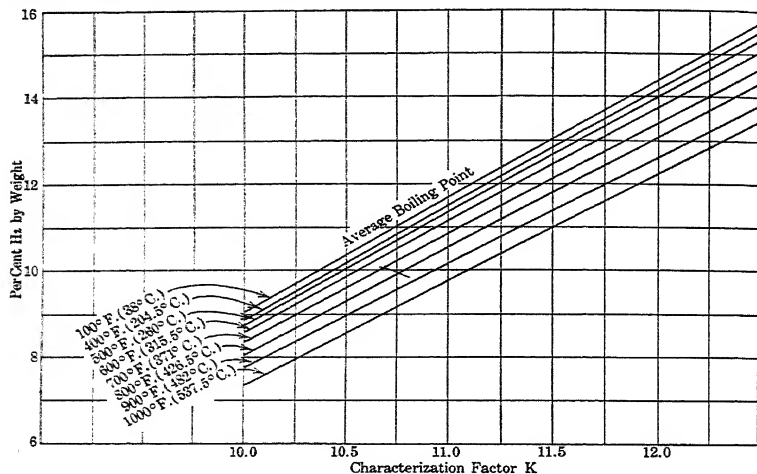


FIG. 38. Characterization Factor vs. Weight % H₂.

with the remainder oxygen, nitrogen, sulphur, and ash. This assumption is unsatisfactory for oils of high sulphur content, such as certain California or Mexican stocks, or where salts are present with water in partial solution and suspension. Specific data should be obtained on such stocks.

Specific Heats — Liquid State. The subject of specific heats of liquid hydrocarbons and petroleum fractions was recently reviewed by Gaucher¹ with the conclusion that the relationship developed by Watson and Nelson² is the most generally satisfactory yet proposed for the data existing at this time. This correlation expresses specific heat as a

¹ Gaucher, Ind. Eng. Chem. **27**, 57 (1935).

² Watson and Nelson, Ind. Eng. Chem. **25**, 880 (1933).

function of specific gravity, temperature, and characterization factor according to the following equation:

$$c_p = 0.6811 - 0.308s + t(0.000815 - 0.000306s)(0.055K + 0.35)$$

where

c_p = specific heat at $t^\circ \text{F}$

s = specific gravity at $60/60^\circ \text{F}$

t = temperature, $^\circ \text{F}$

K = U.O.P. characterization factor

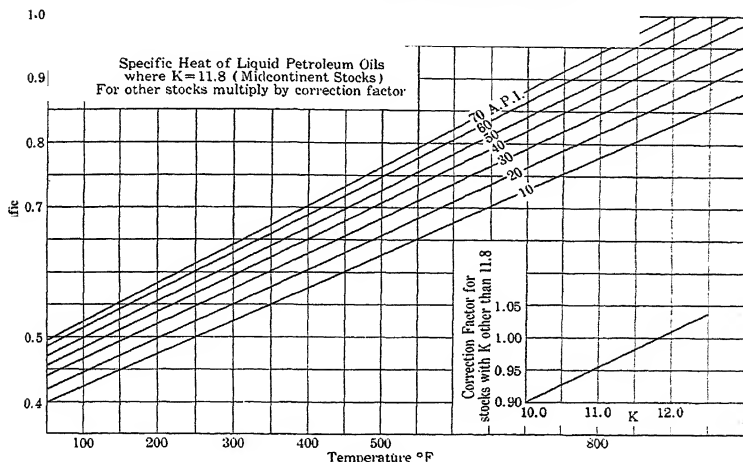


FIG. 39. Specific Heat of Liquid Petroleum Oils Where $K = 11.8$ (Midcontinent Stocks). For Other Stocks Multiply by Correction Factor.

Figure 39 is a plot of the above equation for convenient use. The curves on the main plot apply directly to Midcontinent stocks whose characterization factors are approximately 11.8. For other stocks the value read from the main plot is multiplied by a correction factor derived as a function of K from the small plot in the lower right-hand corner.

Specific Heats — Vapor State. The specific heats of petroleum vapors of Midcontinent stocks have been thoroughly investigated by several laboratories with excellent agreement over wide temperature ranges. On the basis of these data and those available on pure compounds, the following general equation was proposed by Watson and Nelson:

where

- c_p = specific heat at $t^\circ \text{F}$
 s = specific gravity at 60/60° F
 t = temperature, °F
 K = U.O.P. characterization factor

In Fig. 40, specific heats, calculated from the above equation for Midcontinent type petroleum vapors, are represented by the lower curves of the main group, designated according to A.P.I. gravities. The upper

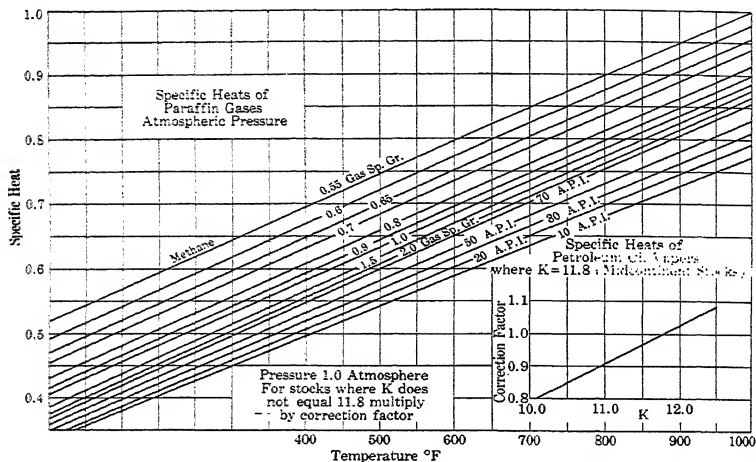


FIG. 40. Specific Heats of Paraffin Gases. Atmospheric Pressure.

curves of the main group, designated by gas specific gravities referred to air as 1.0, represent the data on the paraffin gases. These curves were estimated from the available measurements extrapolated to be consistent with the data on petroleum fractions. For petroleum vapors other than Midcontinent types of 11.8 characterization factor, the values read from the chart are multiplied by a correction factor from the small curve in the lower right-hand corner. This correction is not to be applied to the data on gases.

Heat of Combustion. Average values of heats of combustion of petroleum fractions and hydrocarbons are plotted in Fig. 41 as a function of A.P.I. gravity and characterization factor. These are total heating values, corresponding to formation of liquid water at 60° F.

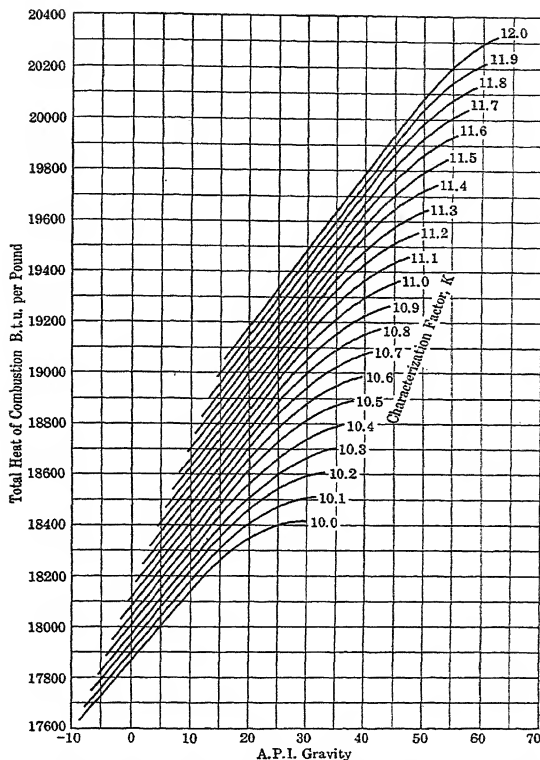


FIG. 41. Total Heats of Combustion of Liquid Petroleum Hydrocarbons.

Illustration 4. A fuel oil has an A. P. I. gravity of 14.1 and a viscosity of 150 Saybolt Furol seconds at 122° F. Estimate the characterization factor, average boiling-point, hydrogen content, specific heat at 200° F, heating value, and average molecular weight of this oil.

From the conversion chart, page 476, it is found that 150 Saybolt Furol seconds is equivalent to 320 centistokes.

- | | |
|---|--------------------|
| a. Characterization factor, Fig. 37 | 11.35 |
| b. Average boiling-point, Fig. 36 or 37 | 880° F |
| c. Hydrogen content, Fig. 38 | 11.5 |
| d. Specific heat 200°, Fig. 39 = 0.485×0.975 | 0.473 |
| e. Average molecular weight, Fig. 36 | 410 |
| f. Heating value, Fig. 41 | 18,825 Btu per lb. |

FUEL GAS

The standard basis which has been adopted for the expression of the total heating value of a fuel gas is the number of Btu evolved when 1 cubic foot of the gas, at a temperature of 60° F, a pressure of 30 inches of mercury, and saturated with water vapor, is burned with air at the same temperature, and the products cooled to 60° F, the water formed in the combustion being condensed to the liquid state. Since gas is rarely burned under these standard conditions of temperature and pressure, the heating value per standard cubic foot is not a convenient unit for calculations. However, the unit is widely used as a basis for specifications and legal standards.

Since the vapor pressure of water at a temperature of 60° F is 0.52 inch of mercury, the heating value per standard cubic foot represents the heating value of 1 cubic foot of moisture-free gas under a pressure of 30 - 0.52 or 29.48 inches of mercury and a temperature of 60° F. The number of mols of moisture-free gas in the standard cubic foot is equal to $1.0 \times \frac{492}{520} \times \frac{29.48}{29.92} \times \frac{1}{359} = 0.002597$ pound-mol. Conversely,

$\frac{1}{0.002597}$ or 385.5 standard cubic feet of fuel gas contain 1 pound-mol of moisture-free gas if the gas behaves ideally.

The heating value of a fuel gas of known composition may be calculated as the sum of the heats of combustion of its components. The necessary data may be obtained from Table XI, page 168. Values of the total heating values of the common combustible gases are also contained in Table XVII, expressed in Btu per standard cubic foot. These values are corrected for deviation from the simple gas law for gases boiling below 60° F.

Fuel gases generally contain complex mixtures of both saturated and unsaturated hydrocarbons. The individual analytical determination of each component of these mixtures is not feasible for ordinary industrial purposes. However, Watson and Ceaglske¹ have described a simple scheme of industrial gas analysis which yields data suitable for ordinary combustion calculations. In this scheme carbon monoxide and hydrogen are separately determined and reported as such. The saturated paraffin hydrocarbon gases are reported in terms of a hypothetical compound C_nH_{2n+2} , representing the average composition of the mixture of paraffins in the gas. Similarly, the unsaturated hydrocarbons or illuminants are reported in terms of a hypothetical compound of average composition, C_2H_3 . For example, the analysis of a gas might be: CO,

¹ Ind. and Eng. Chem., Analytical Ed., January, 1932.

TABLE XVII

HEATING VALUES AND FLAME TEMPERATURES OF GASES

H.V. = total heating value, Btu per standard cubic foot, measured at 30 inches of Hg. and saturated with water vapor.

Gas	Formula	<i>H.V.</i>	Maximum Flame Temperatures with Air at 18° C		
			Theoretical (assuming complete combustion)	Calculated* (allowing for equilibrium conditions)	Actual*
Carbon monoxide	CO	316	2440° C		
Hydrogen	H ₂	319	2200		
Paraffins:					
Methane	CH ₄	1000	1980	1918° C	1880° C
Ethane	C ₂ H ₆	1760	2150	1949	1895
Propane	C ₃ H ₈	2518	2300	1967	1925
Butane	C ₄ H ₁₀	3270	2080	1973	1900
Pentane	C ₅ H ₁₂	4070	2090		
Olefins:					
Ethylene	C ₂ H ₄	1565	2240	2072	1975
Propylene	C ₃ H ₆	2325	2200	2050	1935
Butylene	C ₄ H ₈	3082	2200	2033	1930
Amylene	C ₅ H ₁₀	3900	2180		
Acetylene	C ₂ H ₂	1470			
Aromatics:					
Benzene	C ₆ H ₆	3675	2240		
Toluene	C ₆ H ₅ CH ₃	4410	2240		
Mesitylene	C ₆ H ₃ (CH ₃) ₃	5860	2240		
Naphthalene	C ₁₀ H ₈	5800			

* Jones, Lewis, Friauf and Perrott, J. Am. Chem. Soc. **53**, 869 (1931).

40 per cent; H₂, 42 per cent; C_{2.5}H_{4.2} (illuminants), 7 per cent; C_{1.2}H_{4.4} (paraffins), 11 per cent.

An analysis of this type may be used as effectively for stoichiometric calculations as though all components were individually determined. The heating value of the gas may also be calculated by means of the following approximate formulas for the total heating values of mixtures of paraffins and of unsaturated hydrocarbons.

Paraffin hydrocarbons, C_{*n*}H_{2*n*+2}:

Gram-calories per gram-mol = 158,100*n* + 54,700

Btu per cu ft at 60° F, 30 in., sat.H₂O = 745*n* + 258 (19)

Unsaturated hydrocarbons,

Gram-calories per gram-mol = 98,200*a* + 28,200*b* + 28,800

Btu per cu ft at 60° F, 30 in., sat.H₂O = 459*a* + 132*b* + 135 (20)

If the analysis of a gas is carried out carefully, its heating value may ordinarily be predicted by means of these equations with an error of

less than 2 per cent. Larger errors will arise if large quantities of acetylene are present in the gas.

Illustration 5. A city gas has the following composition by volume:

CO ₂	2.6%
C ₂ H ₄ (unsaturateds)	8.4%
O ₂	0.7%
H ₂	39.9%
CO.....	32.9%
C ₃ H ₈ (paraffins).....	10.1%
N ₂	5.4%
	<hr/>
	100.0%

a. Calculate the theoretical number of mols of oxygen which must be supplied or the combustion of 1 mol of the gas.

b. Calculate the heating value of the gas in calories per gram-mol and Btu per standard cubic foot.

Solution:

a. Basis: 100 gram-mols of gas.

Oxygen required for:

Unsaturateds = $8.4(2.73 + 4.72/4) =$	32.8
Hydrogen = $39.9/2 =$	19.95
Carbon monoxide = $32.9/2 =$	16.45
Paraffins = $10.1(1.14 + 4.28/4) =$	22.3
Total	<hr/> 91.5

Oxygen to be supplied per mol of gas = $0.915 - 0.007 = 0.908$ mol.

b. Basis: 1.0 gram-mol of gas.

Heating value of:

Hydrogen = $0.399 \times 68,310 =$	27,250 cal
Carbon monoxide = $0.329 \times 67,620 =$	22,250 cal
Unsaturateds =	
$0.084 [(2.73 \times 98,200) + (4.72 \times 28,200)$	
$+ 28,800] =$	36,400 cal
Paraffins =	
$0.101 [(1.14 \times 158,100) + 54,700] =$	23,510 cal
Total.....	<hr/> 109,410 cal

Btu per standard cubic foot = $\frac{109,410 \times 1.8}{385.5} = 510$.

Incomplete Combustion of Fuels. The standard heating values of fuels correspond to conditions of complete combustion of all carbon to carbon dioxide gas, hydrogen to liquid water, and sulphur to sulphur dioxide gas. If a fuel is burned in such a manner that complete combustion does not result, the standard heat of reaction may be calculated by subtracting from its standard heating value the standard heats of combustion of the combustible products formed.

Illustration 6. A coal having a heating value of 12,180 Btu per lb and containing 68.1% total carbon is burned to produce gases having the following composition by volume on the moisture-free basis.

CO ₂	12.4%
CO.....	1.2%
O ₂	5.4%
N ₂	81.0%
	<hr/>
	100.0%

Calculate the standard heat of reaction in Btu per pound of coal burned.

Basis: 1.0 lb-mol of flue gas.

C in CO ₂ = 0.124 lb-atom or	1.49 lb
C in CO = 0.012 lb-atom or	0.14 lb
Total carbon = 1.49 + 0.14 =	1.63 lb
Coal burned = 1.63 ÷ 0.681 =	2.39 lb
Heating value of coal = 2.39 × 12,180 =	29,100 Btu
Heat of combustion of CO = 0.012(67,620 × 1.8) =	1460 Btu
Standard heat of reaction = 29,100 - 1460 =	
27,640 Btu or 27,640 ÷ 2.39 =	11,580 Btu
	per lb of coal

TEMPERATURE OF REACTION

Adiabatic Reactions. If a reaction proceeds without loss or gain of equivalent heat and all the products of the reaction remain together in a single mass or stream of materials, these materials will assume a definite temperature known as the *theoretical reaction temperature*. In this particular case, the actual heat of reaction, Q , of Equation (10), page 204, is zero, and it follows that the total relative heat content of the products of the reaction must equal the sum of the standard heat of reaction and the total relative heat content of all the reactants, or the total relative heat input. The temperature of the products which corresponds to this total relative heat content may be calculated by mathematically expressing the heat content of the products as a function of their temperature. This requires data on the heat capacities and latent heats of all products.

The products considered in calculating a theoretical reaction temperature must include all materials actually present in the final system, inerts, and excess reactants as well as the new compounds formed. If the reaction is incomplete, only the standard heat of reaction resulting from the degree of completion actually obtained is considered and the products will include some of each of the original reactants.

The total relative heat content, H , of n mols of any material at a temperature $t^\circ\text{C}$, referred to a temperature of 18°C is expressed by:

$$H = n \int_{18}^t c_p dt + nL \quad (21)$$

where

L = sum of the molal latent heats absorbed in heating from 18°C to $t^\circ \text{C}$ at constant pressure

Expressing the molal heat capacity, c_p , as a parabolic function of temperature, $c_p = a + bt + ct^2$,

$$n \int_{18}^t (a + bt + ct^2) dt + nL \quad (22)$$

Integrating:

$$H = n \left[at + \frac{1}{2} bt^2 + \frac{1}{3} ct^3 \right] + nL \quad (23)$$

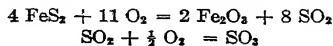
The total relative heat content of each product of a reaction may be expressed by an equation of the form of Equation (23) and all these added together to represent H_p of Equation (10), page 204. The theoretical reaction temperature is then obtained by solution of this equation for t . The solution is generally best carried out graphically.

In all problems dealing with the total heat contents of gases relative to 18°C it may be assumed that the mean heat capacity between 18°C and $t^\circ \text{C}$ is the same as that between 0°C and $t^\circ \text{C}$. The error of this assumption is less than the probable error of the majority of the heat capacity data. On this basis, the mean heat capacity data of Figs. 12 and 14 of Chapter V may be used directly for calculating relative heat contents referred to 18°C .

Illustration 7. For the production of sulphuric acid by the contact process iron pyrites, FeS_2 , is burned with air in 100% excess of that required to oxidize all iron to Fe_2O_3 and all sulphur to SO_2 . It may be assumed that the combustion of the pyrites is complete to form these products and that no SO_3 is formed in the burner. The gases from the burner are cleaned and passed into a catalytic converter in which 80% of the SO_2 is oxidized to SO_3 by combination with the oxygen present in the gases. The gases enter the converter at a temperature of 400°C .

Assuming that the converter is thermally insulated so that heat loss is negligible, calculate the temperature of the gases leaving the converter.

Experimental values of the heat capacity of SO_3 gas are not available. However, it is evident that its heat capacity is greater than that of SO_2 gas because of its greater molecular complexity. The addition of 1 gram-atom of oxygen to form CO_2 from CO increases the molal heat capacity of the oxide of carbon gas by 2 calories. Making this addition to the heat capacity of SO_2 and using approximately the same temperature coefficient the approximate molal heat capacity for SO_3 will be $11.1 + 0.004t$. This value is, of course, only a rough approximation, but a high error in this value will cause but a very slight error in the heat capacity of the gaseous system under consideration because of the relatively high percentages of O_2 and N_2 present.



Basis: 4.0 gram-mols of FeS_2

Oxygen supplied for 100% excess = $11.0 \times 2.0 =$	22 gram-mols
Air introduced = $22/0.21 =$	104.8 gram-mols
N_2 introduced = $104.8 - 22 =$	82.8 gram-mols
Excess O_2 in burner gases = $22 - 11 =$	11.0 gram-mols
SO_2 in burner gases =	8.0 gram-mols

Gases entering converter:

SO_2	8.0 gram-mols
O_2	11.0 gram-mols
N_2	82.8 gram-mols

Total 101.8 gram-mols

SO_3 formed in converter = $8.0 \times 0.8 =$ 6.4 gram-mols

O_2 consumed in converter = $6.4/2 =$ 3.2 gram-mols

Gases leaving converter:

SO_2	6.4 gram-mols
$\text{SO}_3 = 8.0 - 6.4$	1.6 gram-mols
$\text{O}_2 = 11.0 - 3.2$	7.8 gram-mols
N_2	82.8 gram-mols

Total 98.6 gram-mols

Total relative heat content, H_R , of gases entering converter:

Mean heat capacities, 18°C to 400°C , from Fig. 12, page 116 (assuming c_{pm} 0°C to $t^\circ \text{C}$) = $c_{pm}(18^\circ \text{C}$ to $t^\circ \text{C})$.

SO_2 , $c_{pm} =$ 10.0 calories per gram-mol $-^\circ \text{C}$

O_2 , N_2 , $c_{pm} =$ 7.1 calories per gram-mol $-^\circ \text{C}$

Total heat content = $(400 - 18) [(8.0 \times 10.0) + 7.1(82.8 + 11.0)] = 382(80 + 665) = 284,500$ Calories relative to 18°C .

Standard heat of reaction, Q_s :

Heats of formation, from Table X, Chapter VI, page 159.

SO_2 , $Q_F =$ 69,400 calories per gram-mol

SO_3 , $Q_F =$ 91,500 calories per gram-mol

$Q_s = (6.4 \times 91,500) - (6.4 \times 69,400) = 6.4(91,500 - 69,400) = 141,500$ calories.

Total heat input = $H_R + Q_s = 284,500 + 141,500 = 426,000$ calories relative to 18°C .

Total relative heat content, H_P , of products at $t^\circ \text{C}$ (Equation 23):

Heat capacity equations from Table I, page 113.

O_2 and N_2 :

$$H = (82.8 + 7.8) \left[6.94(t - 18) + \frac{0.000677}{2}(t^2 - 18^2) + \frac{0.13 \times 10^{-6}}{3}(t^3 - 18^3) \right] \\ = 629(t - 18) + 0.0306(t^2 - 18^2) + 3.93 \times 10^{-6}(t^3 - 18^3)$$

SO_2 :

$$1.6 \left[9.09(t - 18) + \frac{0.0048}{2}(t^2 - 18^2) \right] \\ = 14.5(t - 18) + 0.00384(t^2 - 18^2) - 0.44 \times 10^{-6}(t^3 - 18^3)$$

SO₂:

$$H = 6.4 \left[1(t - 18) + \frac{0.004}{2}(t^2 - 18^2) \right] \\ = 71(t - 18) + 0.0128(t^2 - 18^2)$$

Adding these equations:

$$H_P = 714.5(t - 18) + 0.0472(t^2 - 18^2) + 3.49 \times 10^{-6}(t^3 - 18^3) \\ = 714.5t + 0.0472t^2 + 3.49 \times 10^{-6}t^3 - 12,865$$

Equating the heat input to the heat content of the products:

$$714.5t + 0.0472t^2 + 3.49 \times 10^{-6}t^3 = 438,865$$

This equation is best solved graphically by the method demonstrated on page 390

$$714.5t + 0.0472t^2 + 3.49 \times 10^{-6}t^3 - 438,865 = \Delta$$

Values of Δ are calculated to correspond to assumed values of t . Plotting Δ against t , the solution of the equation is the value of t where $\Delta = 0$.

Solving: $t = 589^\circ \text{C}$.

For calculating reaction temperatures which are relatively high it may be assumed that the standard heat of reaction at 0°C is the same as that at 18°C . The heat balance from which the reaction temperature is calculated may then be based on 0°C instead of 18°C , permitting effective use of equations for mean heat capacities between 0°C and $t^\circ \text{C}$. This assumption leads to considerable arithmetical simplification and does not introduce appreciable error. Equation (23) becomes

$$H_0 = nt(a_m + b_mt + c_mt^2) + nL \quad (24)$$

where

H_0 = heat content relative to 0°

a_m, b_m, c_m = coefficients of equation for mean heat capacity between 0° and t°

Non-Adiabatic Reactions. If a reaction does not proceed adiabatically, temperature of the reaction may be calculated exactly as in the case of an adiabatic reaction if the amount of heat interchanged between the reacting system and its surroundings is known. The amount of heat lost from the system is equal to Q of Equation (10), page 204, which was assumed to equal zero in calculating the theoretical temperature of an adiabatic reaction. In the general, non-adiabatic case,

$$H_P = H_R + Q_{18} - Q$$

where Q is the heat lost from the reacting system and may be either positive, negative or zero. Consideration of the heat loss from the system does not in any way change the general method used for calculating temperatures of adiabatic reactions.

Theoretical Flame Temperatures. The temperature attained in the complete, adiabatic combustion of a fuel which is thoroughly admixed

with air or oxygen is termed the *theoretical flame temperature*. The methods developed in the preceding sections may be used to calculate the theoretical flame temperature of a gaseous, atomized liquid, or powdered solid fuel when burned with air in any desired proportions. The maximum theoretical flame temperature of a fuel corresponds to combustion with only the theoretically required amount of pure oxygen. The maximum flame temperature *in air* corresponds to combustion with the theoretically required amount of air and is obviously much lower than the maximum flame temperature in pure oxygen. Because of the necessity of using excess air in order to obtain complete combustion, the theoretical flame temperatures of actual combustions are always less than the maximum values.

Illustration 8. Calculate the theoretical flame temperature of a gas containing 20% CO and 80% N₂ when burned with 100% excess air, both air and gas initially being at 18° C.

Basis: 1.0 gram-mol of CO.

Original air-gas mixture:

N ₂ in original gas = $\frac{1}{0.80} \times 0.80 =$	4.0 gram-mols
O ₂ supplied = $0.5 \times 2 =$	1.0 gram-mol
N ₂ from air = $\frac{1.0}{0.79} \times 0.79 =$	3.76 gram-mols
Total N ₂ = $3.76 + 4.0 =$	7.76 gram-mols
Mols of original N ₂ , O ₂ , CO = $7.76 + 1.0$ + 1.0 =	9.76 gram-mols

Combustion products:

CO ₂ formed =	1.0 gram-mol
O ₂ remaining = $1.0 - .5 =$	0.5 gram-mol
N ₂ =	7.76 gram-mols

Heat content of original reactants, H_R (referred to 0° C):

N₂, O₂, CO: (18° C)

$c_{pm}(0 - 18^\circ \text{C}) = 6.94$ (Fig. 12, page 116)

$H_R = 9.76 \times 18 \times 6.94 = 1220$ calories

Standard heat of reaction, Q_s at 0° C (assumed to equal the heat of reaction at 18° C):

From Table XI, page 168

$Q_s = 67,620$ calories

Heat content of products, H_p (referred to 0° C):

O₂, N₂: ($t^\circ \text{C}$)

$c_{pm}(0 - t^\circ \text{C}) = 6.94 + 0.00034t + 0.43 \times 10^{-7}t^2$

$H = t(0.5 + 7.76)(6.94 + 0.00034t + 0.43 \times 10^{-7}t^2)$
 $= 57.4t + 0.00281t^2 + 3.6 \times 10^{-7}t^3$

CO₂: (*t*° C)

$$c_{pm}(0 - t^\circ \text{C}) = 0.09 + 0.0024t - 0.28 \times 10^{-6}t^2$$

$$H = t \times 1.0(0.09 + 0.0024t - 0.28 \times 10^{-6}t^2)$$

$$H^2 = 0.28 \times 10^{-6}t^3$$

Total:

$$H_P = 66.49t + 0.00521t^2 + 0.08 \times$$

Heat balance:

$$67,620 + 1220 = 66.49t + 0.00521t^2 + 0.08 \times$$

Solving this equation graphically,

$$t = 961^\circ \text{C}$$

The theoretical flame temperature of a fuel is dependent on the initial temperature of both the fuel and the air with which it is burned. By *preheating* either the fuel or the air the total heat input is increased and the theoretical flame temperature is correspondingly raised.

Illustration 9. Calculate the effect on the theoretical flame temperature of Illustration 8 of preheating both the gas and air to 1000° C before combustion.

Basis: Same as Illustration 8.

Heat content of original reactants:

N₂, O₂, CO:

$$c_{pm} = (0 \text{ to } 1000^\circ \text{C}) = 7.33 \text{ (Fig. 12, page 116)}$$

$$H_R = 9.76 \times 1000 \times 7.33 = 71,500 \text{ calories}$$

Using the values of *Q_s* and *H_P* found in Illustration 8:

$$67,620 + 71,500 = 66.49t + 0.00521t^2 + 0.08 \times 10^{-6}t^3$$

Solving this equation graphically,

$$t = 1806^\circ \text{C}$$

In Table XVII are values of the *maximum* theoretical flame temperatures of various hydrocarbon gases when burned with air at 18° C.

Actual Flame Temperatures. A theoretical flame temperature is always higher than can be obtained by actual combustion under the specified conditions. There is always loss of heat from the flame, and it is impossible to obtain complete combustion reactions at high temperatures. The partial completion of these reactions results from the establishment of definite equilibrium conditions between the products and reactants. For example, at high temperatures an equilibrium is established between carbon monoxide, carbon dioxide, and oxygen, corresponding to definite proportions of these three gases. Combustion of carbon monoxide will proceed only to the degree of completion which will give a mixture of gases in proportions corresponding to these equilibrium conditions. The general subject of reaction equilibria is discussed in detail in Chapter XIV.

In Table XVII are experimentally observed values of the maximum

flame temperatures of various hydrocarbon gases when burned with air at 18° C. These data are from the work of Jones, Lewis, Friauf and Perrott.¹ These investigators also demonstrated a method of calculating flame temperatures, taking into account the degree of completion actually obtained if the combustion proceeds to equilibrium conditions but neglecting heat loss. The calculated values were ordinarily higher than those experimentally observed. Values of such maximum *calculated* flame temperatures are included in Table XVII.

The maximum values of actual and calculated flame temperatures do not correspond to the air-fuel proportions theoretically required for complete combustion. Because of the incomplete combustion actually produced at high temperatures the maximum flame temperature is obtained with a ratio of air to fuel which is somewhat less than that required for complete combustion.

It will be noted from Table XVII that the maximum flame temperatures of the various gases vary but little. For example, although pentane has twelve times the heating value of hydrogen, its flame temperature is lower by 110° C. This results in the fact that, in the combustion of the gases of high heating values, correspondingly large quantities of combustion products are formed with high total heat capacities.

PROBLEMS

1. Calculate the standard heat of reaction, in Calories, accompanying the reduction of 20 kg of Fe_2O_3 by carbon (coke) to form 12 kg of $\text{Fe}(s)$. The only other products leaving the process are $\text{FeO}(s)$ and $\text{CO}(g)$.

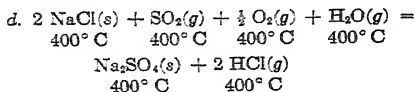
2. By the combustion at constant volume of 2.0 grams of $\text{H}_2(g)$ to form liquid water at 17° C, 67.45 Calories are evolved. Calculate the quantity of heat which would be evolved were the reaction conducted under a constant pressure at 17° C.

3. When 1.0 gram of naphthalene (C_{10}H_8) is burned in a bomb calorimeter, the water formed being condensed, 9621 calories are evolved at 18° C. Calculate the heat of combustion at constant pressure and 18° C, the water vapor remaining uncondensed.

4. Calculate the actual heat of reaction in Calories (kilogram-mols) of each of the following industrial reactions proceeding at atmospheric pressure and the indicated temperature conditions. For the heat capacity of SO_3 see page 226. Assume the mean specific heat of $\text{NaHSO}_4(0 \text{ to } 250^\circ \text{C})$ to be 0.23 and of $\text{Na}_2\text{SO}_4(0 \text{ to } 600^\circ \text{C})$ to be 0.26.

- a. $\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g)$
 450° C 450° C 450° C
- b. $\text{NaHSO}_4(s) + \text{NaCl}(s) = \text{Na}_2\text{SO}_4(s) + \text{HCl}(g)$
 250° C 30° C 600° C 300° C
- c. $\text{SiO}_2(s) + 3 \text{C}(s) = \text{SiC}(s) + 2 \text{CO}(g)$
 18° C 18° C 1800° C 1200° C

¹ J. Am. Chem. Soc. **53**, 869 (1931).



5. Calculate the general equation expressing the molal heat of combustion at constant pressure, in calories per gram-mol, of hydrogen at any constant temperature $T^\circ \text{K}$, the water remaining uncondensed.

6. Sulphur dioxide gas is oxidized in 100% excess air with 80% conversion to SO_3 . The gases enter the converter at 400°C and leave at 450°C . How many Calories are absorbed in the heat interchanger of the converter per kilogram-mol of SO_2 introduced?

7. Calculate the heat of neutralization in calories per gram-mol of $\text{NaOH}(n_1 = 5)$ with $\text{HCl}(n_1 = 7)$ at 25°C .

8. A bed of petroleum coke (pure carbon) weighing 3000 kg, at an initial temperature of 1300°C , has saturated steam at 100°C blown through it until the temperature of the bed of coke has fallen to 1000°C . The average temperature of the gases leaving the generator is 1000°C . The analysis of the gas produced is CO_2 , 3.10%; CO , 45.35%; H_2 , 51.55% by volume, dry basis. How many kilograms of steam are blown through the bed of coke to reduce the temperature to 1000°C ? Neglect loss of heat by radiation and assume that no steam passes through the process undecomposed.

9. In Problem 8, 20% of the steam passes through the coke undecomposed. How much steam is blown through the bed of coke to reduce its temperature to 1000°C ? Neglect loss of heat by radiation.

10. Steam at 200°C , 50° superheat, is blown through a bed of coke initially at 1200°C . The gases leave at an average temperature of 800°C with the following composition by volume on the dry basis:

H_2	53.5%
CO	39.7%
CO_2	6.8%
	<hr/> 100.0%

Of the steam introduced 30% passes through undecomposed. Calculate the heat of reaction in Calories per kilogram-mol of steam introduced. Mean specific heat of coke (0 to 1200°C) = 0.35.

11. Calculate the number of Btu which is required to completely calcine 100 lb of limestone containing 80% CaCO_3 , 11% MgCO_3 , and 9% H_2O . The lime is withdrawn at 1650°F and the gases leave at 400°F . The limestone is charged at 70°F .

12. Limestone, pure CaCO_3 , is calcined in a continuous vertical kiln by the combustion of producer gas in direct contact with the charge. The gaseous products of combustion and calcination rise vertically through the descending charge. The limestone is charged at 18°C and the calcined lime is withdrawn at 900°C . The producer gas enters at 600°C and is burned with the theoretically required amount of air at 18°C . The gaseous products leave at 200°C . The analysis of the producer gas by volume is as follows:

CO_2	9.21%
O_2	1.62%
CO	13.60%
N_2	75.57%
	<hr/> 100.00%

Calculate the number of cubic meters (0°C , 760 mm Hg) of producer gas, required to burn 100 kg of limestone, neglecting heat losses and the moisture contents of the air and producer gas.

13. A fuel gas of the following composition at 1600°F is burned in a copper melting furnace with 5% excess air at 65°F .

CH_4	40%
H_2	40%
CO	4%
CO_2	3%
N_2	11%
O_2	2%
	<hr/> 100%

The copper is charged at 65°F and poured at 2000°F . The gaseous products leave the furnace at an average temperature of 1000°F . How much copper is melted by burning 4000 cu ft (32°F ; 29.92 in. Hg; dry) of the above gas, assuming that the heat lost by radiation is 50,000 Btu and neglecting the moisture contents of the fuel gas and air?

14. One thousand cubic meters of gas, measured at standard conditions (0°C , 760 mm and dry), containing 20 grams of ammonia per cubic meter (as measured above) are passed into an ammonia absorption tower at a temperature of 40°C , saturated with water vapor, and at a total pressure of 740 mm. The gas is passed upward countercurrent to a descending stream of water which absorbs 95% of the incoming ammonia. The gas leaves the tower at 38°C , saturated with water vapor. Six hundred kilograms of water enter the top of the tower at 20°C . What is the temperature of the solution leaving the tower, neglecting heat losses? Assume the mean molal heat capacity of moisture-free, ammonia-free gas to be 7.2 Calories per kilogram-mol $^{\circ}\text{C}$.

15. Pure HCl gas comes from a Mannheim furnace at 300°C . This gas is cooled to 60°C in a silica coil and is then completely absorbed by passing it countercurrent to a stream of aqueous hydrochloric acid in a series of Cellarius vessels and absorption towers. The unabsorbed gas from the last Cellarius vessel enters the first absorption tower at 40°C . Fresh water is introduced in the last absorption tower at 15°C and leaves the first absorption tower at 30°C containing 31.45% HCl (20°Bé acid). This acid is introduced into the last Cellarius vessel and leaves the first vessel at 30°C containing 35.21% HCl (22°Bé acid). There are produced in this system 9000 lb of 22°Bé acid in 10 hours. Calculate separately the heat removed in the cooling coil, Cellarius vessels, and absorption towers, neglecting the presence of water vapor in the gas stream and assuming complete absorption of HCl.

16. A Kentucky coal has the following analysis:

<i>Proximate Analysis as Received</i>		<i>Ultimate Analysis of Combustible Corrected ash-free, moisture-free basis</i>	
Moisture.....	2.97%	C.....	84.39%
Ash (uncorrected) ..	2.94%	Net hydrogen.....	4.81%
Volatile matter.....	37.75%	N_2	2.00%
Fixed carbon.....	56.34%	S.....	1.02%
		Combined H_2O	7.78%
	<hr/> 100.00%		<hr/> 100.00%

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The combustible referred to above includes those portions of the coal as received which are not classified as moisture or *corrected* ash.

Determine, on the "as received" basis:

- The rank of this coal.
- The total heating value by Dulong's formula.
- The total heating value by Uehling's method.
- The estimated available hydrogen content by Uehling's method.
- The net heating value by Uehling's method.
- Ultimate analysis (as received, corrected ash).

17. A gas has the following composition by volume

Illuminants (C_2H_4 and C_6H_6)	53.6%
O_2	1.6%
CH_4	16.9%
C_2H_6	24.3%
N_2	3.6%

The heating value of this gas is 1898 Btu per standard cubic foot. Calculate the percentages of C_2H_4 and C_6H_6 in the gas.

18. Calculate the maximum theoretical flame temperature in degree Centigrade when the following gas is burned with the theoretical amount of dry air starting with air and gas at $18^\circ C$.

CO	30%
H_2	15%
O_2	1%
CO_2	5%
N_2	49%
	<hr/> 100%

19. Calculate the theoretical flame temperature when the above gas is burned with 100% excess air.

20. Calculate the theoretical flame temperature of the above gas when burned with the theoretical amount of air and when both gas and air are preheated to $500^\circ C$ before combustion.

21. Calculate the theoretical flame temperature of the above gas when burned with the theoretical amount of air, the combustion of both CO and H_2 proceeding to only 80% completion. The gas and air are initially at $18^\circ C$.

22. Four thousand kilograms of coke at an initial temperature of $1400^\circ C$ has 360 kg of steam blown through it, forming 448 kg CO, 88 kg CO_2 , and 40 kg H_2 at an average temperature of $1000^\circ C$. The steam is supplied at $120^\circ C$, saturated. The radiation loss is 100,000 Calories. Calculate the final temperature of the bed of coke.

23. A fuel gas has the following composition by volume:

CO_2	2.1%
O_2	0.5%
$C_{2.5}H_{4.5}$ (illuminants)	7.0%
CO	33.8%
H_2	40.6%
$C_{1.5}H_{4.4}$ (paraffins)	11.2%
N_2	4.8%
	<hr/> 100.0%

- a. Calculate the analysis of the flue gases formed by burning this gas with 30 per cent excess air, assuming that all combustible components are burned to CO_2 and H_2O .
 - b. Calculate the heating value in Btu per standard cubic foot.
24. A fuel oil has a specific gravity of 0.91 and a viscosity of 28 Saybolt Furol seconds at 122. Estimate the characterization factor, average molecular weight, average boiling-point, hydrogen content, specific heat at 150° F, and heating value of this oil.

CHAPTER VIII

WEIGHT AND HEAT BALANCES OF COMBUSTION PROCESSES

HEAT BALANCES

In establishing a heat balance all sources of thermal energy are entered on the input side of the balance and all items of heat utilization and dissipation on the output side. It is ordinarily desirable to base all thermal quantities on a reference temperature of 18°C , thus permitting direct use of standard thermochemical data. Other reference temperatures may be used if desired, but in any event it is necessary that each complete balance be based on a single constant-reference temperature.

Where a fuel is used in an industrial reaction two different points of view are emphasized in establishing a heat balance, depending upon whether or not the fuel is intended primarily as a source of heat or principally as a reducing agent. In the first instance the entire heating value of the fuel is listed on the input side of the balance and the entire heating value of the products resulting from the partial combustion of the fuel and its reaction with the charge on the output side. In this instance the utilization of the heating value of the fuel is of principal interest for heating purposes or in producing a fuel gas which is subsequently to be used for heating. In the second instance, where fuel is used primarily as a reducing agent, as in the reduction of ores, the principal interest is in the products of reduction and not in the heating value of the fuel or of the products of reaction. In this latter instance it is customary to include on the input side of the heat balance the heat evolved in the partial combustion of the fuel, which represents the difference between the heating value of the fuel and the heating value of the combustible products resulting from the incomplete combustion of that fuel.

With these two points of view in mind, the input and output items of a heat balance of a chemical process, based upon a reference temperature of 18°C , are distributed in the following classification.

INPUT ITEMS

Group 1. The total relative heat content, both sensible and latent, of each material entering the process.

Group 2. Where fuel is used primarily as a source of heat or in the production of fuel gases, the total heating value of the fuel.

- Group 3. The heat evolved at 18° C in the formation of each final product from the initial reactants when such heat effects are exothermic. Where a fuel is used and its total heating value is debited the products formed from the fuel by combustion or reaction of the fuel with the charge are not considered in this group since their heating values were already included in Group 2.
- Group 4. All quantities of heat supplied directly to the process from external sources in the forms of heat, electrical or radiant energy.

OUTPUT ITEMS

- Group 1. The total relative heat content of each material leaving the process.
- Group 2. Where fuel is used primarily as a source of heat or in the production of fuel gases the total heating value of each product resulting from the partial combustion of the fuel and its reaction with the charge.
- Group 3. The heat absorbed at 18° C in the formation of each final product from the initial reactants when such heat effects are endothermic. Where the total heating value of the fuel is debited the products formed from the fuel are not considered in this group.
- Group 4. All equivalent heat transferred from the process for useful purposes as for the generation of steam in a boiler furnace.
- Group 5. All energy lost from the process in the form of heat, electrical, or radiant energy.

The difference between input group 2 and output group 2 merely represents the difference between the heating value of the fuel and the heating value of the products of incomplete combustion of that fuel and is considered entirely as one of the items in input group 3 when the fuel is used primarily as a reducing agent. Equating the sums of the input and output items merely results in an elaboration of Equation (10) of Chapter VII. Separate consideration of the heating value of the fuel and of its products in no way changes the validity of Equation (10) but is made in order to produce a heat balance of greater economic significance.

In establishing a heat balance it would also be permissible to place on the input side the heats of formation of all components in the initial charge and to place on the output side the heats of formation of all components of the final products. However, such a heat balance might ordinarily be extremely distorted since it would take into consideration the chemical energy of all materials which pass through the process unchanged and would include the heats of formation of all materials involved.

A heat balance will show how much energy is consumed by necessary endothermic reactions, how much is transferred to a heat interchanger or stored in a fluid used for supplying useful heat or power, and how much heat is wasted owing to incomplete combustion of fuels, to overheating of products, and to inadequate thermal insulation. From the

analysis of a heat balance it is possible to locate the causes of low thermal efficiency, to determine the items in which economies in operation are to be sought, the value of thermal insulation, the possibilities of recovering waste heat, and points where redesign in construction or improvement in methods of operation may effect greater economy, higher efficiency, and more uniform quality.

For example, in a boiler furnace a heat balance will indicate the distribution of the chemical energy of the coal into the heat energy of steam, the amount of heat lost in the gaseous products due to the presence of combustible gases and to sensible heat, the heat loss due to incomplete combustion of coal as represented by the unburned coke and coal in the refuse and the loss of heat by radiation and conduction through the boiler setting. The justification of further insulation, of increasing the size of the combustion space, of increasing the draft, and of using automatic stoking can be answered, at least in part, from the study of such a heat balance.

Heat Content of Water Vapor. Much confusion and loose usage have existed in the treatment of the heat contents of water vapor and liquid water in the calculation of heat balances. In order to be consistent with the generally accepted definition of heat content and to maintain the scientific basis of the equality of the heat balance, the heat content of water must always be included in a heat balance as the total relative heat content at constant pressure, referred to liquid water at 18°C . For superheated water vapor this total heat content is the sum of three separate items:

1. The sensible heat content of the water in the liquid state at the saturation-point of the vapor. This item may be either positive or negative, depending on whether the saturation-point is above or below 18°C .
2. The latent heat of vaporization of the water at the saturation temperature.
3. The sensible heat content of the water vapor referred to the saturation temperature.

For the sake of consistency the heat content of water vapor will be determined in this manner in all heat balances developed in the following pages. However, where water vapor is highly superheated, as in flue gases, it is general practice to simplify this calculation by assuming that the heat content of water vapor is equal to the sum of the latent heat of vaporization at 18°C plus the sensible heat content of the vapor referred to 18°C . In effect, this is assuming a saturation temperature of 18°C for the water vapor. Where the amounts of water vapor are small or where it is highly superheated this assumption leads to no appre-

ciable error, but it should be recognized as an inexact approximation and used accordingly.

Reference Temperature. In order to make direct and rigorously correct use of standard heat of reaction data a heat balance must be based on a reference temperature of 18°C (64.4°F). However, in many processes a majority of the materials enter at the average temperature of the surrounding atmosphere, which may be somewhat different from 18°C . If the heat balance is referred to 18°C the heat content of each of these materials must be included on the input side of the balance. Where many materials enter a process at about the same temperature, t_0 , which is but little different from 18°C , considerable simplification results from choosing t_0 as the reference temperature of the heat balance. On this basis the heat content of the materials entering at t_0 will be zero. In working from a reference temperature, t_0 , other than 18°C , it is assumed that the standard heats of reaction at t_0 are the same as at 18°C . The error of this assumption is ordinarily negligible for values of t_0 between 0°C and 35°C .

THERMAL EFFICIENCY

The thermal efficiency of any process is defined as the percentage of the total heat input which is effectively utilized in the desired manner. It is evident that the thermal efficiency of a process may be expressed in a number of different ways, depending on the method of designating the total heat input and the effectively utilized heat. In stating a value of thermal efficiency it is always necessary to specify completely the basis upon which it was calculated.

The total heat input on which the efficiency is based may be taken as the total of the input items of the heat balance. This would seem to be the most logical basis for general usage, and unless otherwise specified thermal efficiencies will be considered as on this basis and termed thermal efficiencies based on *actual heat* input. However, many special bases are in common use to fit the needs of particular processes. In expressing the thermal efficiency of a combustion process it is customary to obtain the total heat input by deducting from the input items of the heat balance the latent heat of vaporization, at 18°C , of the water vapor present in the air used for combustion. On this basis the thermal efficiency is termed the thermal efficiency *based on total heating value*.

Because of the fact that in many combustion processes water will not be condensed from the products of combustion, even if they are cooled to 18°C , it is sometimes considered that the thermal efficiency of the apparatus should be based on the net heating value of the fuel. The total heat input is then obtained by considering only the net heating

value of the fuel, plus all the sensible heat supplied. A thermal efficiency on this basis is termed the thermal efficiency *based on the net heating value*. This method of expression has as its principal advantage the fact that the percentage efficiencies are higher and appear more encouraging. However, it is undesirable because combustion apparatus is available which is capable of recovering some of the latent heat of the water vapor from the gaseous products. On this basis of expression such apparatus might have an efficiency above 100 per cent. The thermal efficiency based on total heating value is a better general criterion for judging the operation of a combustion process.

Percentage efficiency is also dependent on the quantity of heat which is designated as effectively utilized. Various interpretations frequently may be made of this quantity. For example, a furnace and steam boiler unit used in domestic heating might be considered as effectively utilizing only the heat represented by the heat content of the steam produced. On the other hand, it might be logical to include as effective heat the radiation from the furnace itself which is used in heating the room in which it is situated. The efficiency of the unit might be expressed on either basis.

A gas producer or water gas generator produces a combustible gas at a relatively high temperature. If the gas can be utilized while hot its sensible heat content as well as its heating value should be included in the effectively utilized heat of the producer unit. The efficiency of the unit on this basis is termed the *hot thermal efficiency*. If the gas must be cooled before use its sensible heat is not useful and only the heating value can be classed as heat effectively utilized in the producer. The efficiency on this basis is termed the *cold thermal efficiency*.

WEIGHT BALANCES

Calculation of the quantities of energy involved in a process requires a prior knowledge of the weights, temperatures, states of aggregation, and chemical compositions of all materials involved. A necessary antecedent to a heat balance is therefore a knowledge of the material distribution in the process. An accurate accounting of all the materials charged into a process and the products and by-products resulting therefrom is known as a *weight balance*. In a weight balance the weights of all materials charged into the process are balanced against an output of all products and by-products of that process.

In establishing a weight balance it is usually necessary to know not only the total weights involved but also the chemical composition of all streams of charges, products, and by-products, in order that a separate weight balance of each constituent element may be calculated. This is

particularly necessary where chemical transformations have taken place and is essential in calculating the changes in chemical energy involved. In establishing the weight balance of a boiler furnace, the analysis of the fuel burned, the carbon content of the refuse, and the composition of the outgoing gases are required. In metallurgical processes the chemical analyses of ores, coke, metals, and gases must be known before correct weight and heat balances can be established.

It may not be possible or convenient nor is it necessary to measure directly the weights of all streams of charges, products, and by-products and to determine experimentally the composition of each material. From direct experimental data on the weights and chemical compositions of a few streams it is possible to calculate the weight and chemical composition of others. For example, the weights of gaseous products from a given weight of fuel in a combustion process can be calculated from a determination of the carbon content of the fuel and the chemical analysis of the gases. The weight and composition of a furnace slag can be estimated from the weight and composition of ore and flux charged and gases evolved. It is generally desired to determine a complete material balance by calculation from a minimum number of experimental data. By so doing it is possible to avoid the direct measurement of many quantities which could be experimentally determined only with great difficulty and expense. For example, it is very difficult to measure directly the quantity of air which is taken into a furnace or kiln or the quantity of the products of combustion which are discharged therefrom. Similarly, certain analyses, such as the determination of hydrogen in coal, are difficult and to be avoided if possible. In the calculation of complete material balances from relatively few actual measurements the principles of the preceding chapters are essential.

The solutions of many of the illustrations and problems in the preceding chapters constitute material balances of simple processes or parts of processes. For example, in the combustion of pure sulphur with dry air a complete material balance is represented by a statement of the quantity and composition of the air used and of the gases produced per unit weight of sulphur burned. In this process materials enter in two streams and leave in one. The material balance of a simple drying process is complete with a knowledge of the quantities of gases entering and leaving and the weight of liquid evaporated per unit weight of material being dried. In this case materials enter the process in two streams and leave in two, the gases and the dried materials. For the calculation of more elaborate balances exactly the same principles are used successively and in combination. Most fundamental of all is the principle of the conservation of mass, from which it follows that the

quantity of each element entering a process must be exactly equal to the sum of the quantity of this element which leaves the process plus that which remains in it.

General Method of Calculations. The evaluation of the material balance of a complicated process offers a problem the solution of which requires an essentially different procedure for each particular type. Such solutions must be built up, step by step, in a manner dependent on the data available. Few general rules of procedure exist, and the calculator is forced to depend almost entirely upon his ability to analyze the problem into its elementary parts, to recognize the starting-point, and to make proper use of fundamental principles.

Flow-Charts. The ability to visualize completely the process under consideration is of prime importance in analyzing any problem concerning it. This visualization often may be facilitated by the preparation of a detailed, diagrammatic *flow-chart*. On such a chart each major piece of equipment may be represented by a rectangle inside which is a complete designation of its significance. The various streams of materials passing through the process are indicated by lines with arrows to indicate the directions of travel. A description of each stream of material, and its analysis if desired, may be attached to these directional lines. Typical flow-charts accompany each illustration of a weight balance in this chapter. By carefully preparing these charts with the apparatus in the proper relative positions and sequence, even very complicated processes may be readily visualized. Such a diagram also offers a useful means for the presentation of the final results of a material balance by including the quantity and complete composition in the description of each stream of materials. It is recommended that flow-charts be prepared of all except the most simple processes before it is attempted to calculate either a material or heat balance.

Chemical analyses of materials are more readily determined than are measurements of quantity, especially where gases are involved. For this reason the typical problem in the evaluation of a material balance is one in which experimentally determined analyses or partial analyses are available for all the streams of materials entering and leaving the process. The major problem of calculation is then to determine the relative quantities of the various streams. Two general rules may be stated regarding the information which must be available before such calculations may be carried out:

1. The relative quantities of two streams of materials of known analyses, one of which enters and the other leaves a process, may be calculated if any one element passes through the process in such a way that a

known fraction of its total quantity is present in each of the streams under consideration.

2. The relative quantities of two streams of materials of known analyses may be calculated if one stream contains a material of which a known fraction is consumed, produced, or combined through reaction with a known fraction of the total quantity of some material of the other stream.

If the data required by either of these rules are not initially available they frequently may be determined by means of a preliminary balance of the total quantities of some particular element or compound entering and leaving the process. Thus, if a known total quantity of an element enters, exactly the same quantity of it must leave if there is not retention of material in the process. From this known total quantity of the element it is possible to determine, by difference, the amount of it which is present in any one of the streams of material which leave the process if the sum of the amounts present in all the other streams is known. Complicated material balances must be worked out by a series of such individual balances of the quantities of various elements or compounds present. From such balances sufficient information may be obtained for the requirements of one of the two rules given above, permitting calculation of the relative quantities of two of the streams of materials. When these relative quantities are known additional balances may be made, leading to information from which the relative quantities of other streams may be determined. In this way solutions may be built up, step by step, but a different detailed procedure is required for each particular problem.

In the following sections several typical material balances of familiar processes are calculated. It is intended that these illustrations shall serve as a guide in the development of the analytical sense required for such solutions. The illustrations also demonstrate methods which should be of direct practical value to those called on to deal with the particular processes treated. However, little educational benefit can be derived by treating these solutions merely as forms according to which other problems of identical natures may be solved by the mere substitution of numbers. No collection of such calculation forms could meet all the diversified problems which arise in industrial practice, and the engineer who must depend on a form to guide his reasoning is greatly handicapped in his training.

COMBUSTION OF FUELS

In calculating the weight and heat balances of processes involving the partial or complete combustion or decomposition of fuels, the same prin-

ciples are employed whether such fuels are gaseous, liquids, or solid. The weight balance of a simple combustion process includes the weights of fuel and air supplied and the weights of refuse and gases produced. This weight balance can be calculated completely from a knowledge of the chemical composition of the four items mentioned without any direct measurements of the weights except the weight of fuel consumed. In the weight balance it is convenient to consider water vapor in separate entries because water vapor always requires a separate determination and is subject to variations dependent upon weather conditions. The weights (or volumes) of air and gaseous products are usually not measured because of the great difficulties involved and because these can usually be calculated indirectly with even greater accuracy than by direct measurement.

In the burning of coal on a grate as in a boiler furnace the weight and composition of fuel used and composition of gaseous products are measured directly. The chemical analysis of the fuel should include the percentages of carbon, hydrogen, oxygen, moisture, nitrogen, and ash. It may not be necessary to have a complete ultimate analysis, but in any event the carbon, moisture, and ash content should be known. A complete analysis of the dry gaseous products is always necessary. The moisture content in the gaseous products can be calculated, provided the hydrogen content of the fuel is known, or can be determined by measuring the dew-point of the gas.

The refuse from the furnace may be considered as consisting of ash, coked carbon, and unchanged combustible matter from the coal. The composition in terms of these constituents may be estimated from a determination of ash, fixed carbon, and volatile matter in the refuse, using the standard scheme of proximate analysis. The weight of refuse actually formed per unit weight of coal should be calculated on the basis of the *ash* contents of refuse and coal, as reported in the proximate analysis, and not on the basis of the *corrected ash* reported in the ultimate analysis.

The air entering the furnace may be assumed to be of average atmospheric composition and its humidity determined by a psychrometric method. The analysis of the flue gases is ordinarily determined by the Orsat type of apparatus, yielding the percentages of carbon dioxide, carbon monoxide, oxygen, and nitrogen in the *moisture-free* gases. For more nearly accurate work, determinations of methane and hydrogen should also be made.

Weight and heat balances of combustion processes are based either upon a unit weight of fuel or upon the weight of fuel used in a given cycle or unit time of operation. For example, in boiler furnaces operating

continuously the analysis can be based on a period of twenty-four hours or reduced to a basis of one pound of coal consumed. In operating a ceramic kiln of the batch type the analysis should be conducted over a complete cycle of operation including time of preheating and firing and the final results based on the entire cycle of operation.

When sufficient experimental data are collected the same scheme of calculations may be employed for all problems in combustion. However, complete information is seldom available and it becomes necessary to devise methods of circumventing these limitations. Since it is less costly to calculate information than to obtain it by experimentation, many solutions of combustion problems are built on various assumptions with a limited amount of data. A compromise must be made sacrificing a certain degree of precision for the sake of experimental economy. Extensive information can often be built up from but few data, and complete weight and heat balances established from a few temperature measurements, the proximate analysis of coal, and an Orsat analysis of gas.

The various calculations which follow illustrate the modifications in procedure necessary to make the best use of data available and also to deal with the special variations in combustion processes represented in five special cases.

Case 1. Combustion of coal in a boiler furnace where:

- a. Complete ultimate analysis of fuel is known.
- b. No uncoked coal appears in refuse.
- c. Tar and soot are negligible.
- d. Sulphur is negligible.

Case 2. Combustion of coal where:

- a. Hydrogen and nitrogen contents are unknown.
- b. Uncoked coal drops into refuse.

Case 3. Combustion of coal where sulphur is not negligible.

Case 4. Partial combustion of fuel, as in a gas producer, where:

- a. Steam is admitted.
- b. Tar and soot are not negligible.

Case 5. Combustion of a gaseous fuel.

Case 1. Combustion of Coal in Boiler Furnace. The simplest problem in combustion will be considered first where complete information is available or can be directly estimated on the ultimate analysis of coal, where tar and soot in the gases are negligible, where the sulphur content of the fuel is negligible, and where no uncoked coal drops into the refuse. The methods employed in this illustration are entirely

general and may be similarly applied to all problems in the combustion or partial combustion of a carbonaceous fuel whether solid, liquid, or gaseous.

The weight balance of a furnace is represented by the following items.

Input

1. Weight of fuel charged.
2. Weight of dry air supplied.
3. Weight of moisture in air supplied.

Output

1. Weight of dry gaseous products.
2. Weight of water vapor in gaseous products.
3. Weight of refuse.

The method of calculating each of these items will be discussed in detail. General methods for such calculations have already been discussed in Chapters I to IV.

Illustration 1. From a 12-hour test conducted on a coal-fired steam generating plant the following data were obtained.

Data on Coal Fired

Ultimate analysis

Carbon.....	65.93%
Available hydrogen.....	3.50%
Nitrogen.....	1.30%
Combined water.....	6.31%
Free moisture.....	4.38%
Ash.....	18.58%
Total.....	100.00%
Total heating value =	11,670 Btu per lb
Total weight of coal fired =	119,000 lb
Average temperature of coal.....	65° F

Data on Refuse Drawn from Ash Pit

Ash content =	87.4%
Carbon content.....	12.6%
Average temperature.....	255° F
Mean specific heat from 65 to 255° F.....	0.23

(Estimated from Fig. 22, page 127)

Data on Flue Gas

1. Orsat analysis (average of analyses made every 15 minutes)

Carbon dioxide.....	11.66%
Oxygen.....	6.52%
Carbon monoxide.....	0.04%
Nitrogen.....	81.78%
Total.....	100.00%
Average temperature.....	488° F

Data on Air

Average dry-bulb temperature.....	73.0° F
Average wet-bulb temperature.....	59.4° F
Average barometric pressure = 29.08 in. Hg	

Data on Steam Generated

Average feed water temperature.....	193° F
Weight of water evaporated.....	1,038,400 lb
Average steam pressure = 137.4 lb per sq in. gauge	
Average moisture content of steam.....	1.7%

Calculate the weight and heat balances for the entire plant.

WEIGHT BALANCE

All calculations are based upon 100 lb of coal as fired.

1. Weight of Refuse Formed.

Where the refuse is not weighed directly its weight can be readily calculated from its ash content and that of the coal. The following method is correct where mineral sulfides are not present in the coal.

Ash content of coal.....	18.58 lb
Ash content per pound of refuse.....	0.8740 lb
Weight of refuse formed = $\frac{18.58}{0.8740}$ =	21.2 lb

2. Weight of Dry Gaseous Products.

A direct measurement of the weight of gaseous products from a combustion process is seldom made because of the many difficulties involved. Pitot tubes measure inaccurately because of the low velocities encountered in chimneys and flues. Orifice and Venturi meters are similarly unreliable because of low-pressure drops encountered and because soot accumulates in the openings. Electric flow meters read inaccurately if the composition of the gas varies with respect to carbon dioxide or water vapor. In any case the direct measurement of gas streams is made extremely difficult because of variation in temperature and velocity across each section of the stream. Any accurate measurement must give a correct integrated value of velocity and temperature over the entire cross section. Because of these uncertainties and troubles it becomes easier and more accurate to calculate the weight of gaseous products from the stoichiometric relationships of combustion.

The complete analysis of the gaseous products includes the percentages of carbon dioxide, carbon monoxide, oxygen, methane, ethane, hydrogen, and nitrogen present. Moisture content is not revealed in the usual gas analysis because the entire analysis is conducted with the gas sample saturated with water vapor at a constant temperature and pressure.

The general rule is recommended that the *weight of dry gaseous products should be calculated from a weight balance of carbon.* A carbon bal-

ance is selected as the basis of this calculation for two reasons. In the first place, carbon is determined with a higher degree of precision in both fuel and gaseous products than any other element present. Secondly, carbon is the chief constituent in both fuel and gaseous products so that a slight error in its determination will not be magnified in subsequent calculations. To calculate the weight of gaseous products from a weight balance of any other element would invite many additional sources of error. For example, the hydrogen balance would be entirely out of the question because of the many sources of hydrogen, its relatively low percentage content, its several outlets, and its various methods of combination. Hydrogen comes from the coal as moisture, combined water, and as available hydrogen, and from the air used for combustion as water vapor. The hydrogen leaves combined with carbon and with oxygen in the gaseous products as well as in the unburned fuel. Similarly the weight of gaseous products cannot be calculated upon the basis of oxygen or nitrogen since these elements come chiefly from air and their presence in the fuel is small and not accurately known.

Carbon Balance

Carbon gasified. *Basis:* 100 lb coal fired.

Carbon in coal = $100 \times 0.6593 =$	65.93 lb or 5.49 lb-atoms
Carbon in refuse = $21.2 \times 0.1260 =$	2.67 lb or 0.22 lb-atoms

Carbon entering gases =	63.26 lb or 5.27 lb-atoms
-------------------------	---------------------------

Carbon in gases. *Basis:* 1.0 lb-mol of gas.

Carbon in $\text{CO}_2 =$	0.1166 lb-atom
Carbon in CO =	0.0004 lb-atom

Total carbon =	0.1170 lb-atom
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Mols of dry stack gas per 100 lb coal fired

$$= 5.27/0.1170 = 45.1 \text{ lb-mols}$$

Total dry gaseous products. *Basis:* 100 lb coal fired.

$\text{CO}_2 = 45.1 \times 0.1166 =$	5.26 lb-mols or $\times 44 =$	231.5 lb
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$\text{CO} = 45.1 \times 0.0004 =$	0.018 lb-mol or $\times 28 =$	0.506 lb
------------------------------------	-------------------------------	----------

$\text{O}_2 = 45.1 \times 0.0652 =$	2.94 lb-mols or $\times 32 =$	94.2 lb
-------------------------------------	-------------------------------	---------

$\text{N}_2 = 45.1 \times 0.8178 =$	36.90 lb-mols or $\times 28.2 =$	1041 lb
-------------------------------------	----------------------------------	---------

Total.....	45.1 lb-mols	1367 lb
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Average molecular weight = $1367/45.1 =$	30.3
--	------

3. Weight of Dry Air Supplied.

Direct measurement of the weight or volume of air used in combustion is accompanied by the same difficulties as the direct measurement of gaseous products. Furthermore, air is usually drawn through the

¹ The molecular weight of atmospheric "nitrogen" is taken as 28.2 because of the argon associated with it.

grate by chimney draft so that there is no need for confining the supply of air in ducts and there is no opportunity for direct measurement of its flow.

The dry air used in combustion consists of oxygen and inert gases, chiefly nitrogen. These inert gases also include argon and traces of rare gases, but because of the small amount present it is customary to include all the inert gases as nitrogen and assign a molecular weight of 28.2 to atmospheric "nitrogen." This nitrogen passes through the furnace unchanged and appears entirely in the gaseous products. Any nitrogen present in the fuel burned will also appear in the flue gases. The nitrogen in ordinary solid and liquid fuels burned will usually be negligible or very small. However, in the combustion of gases a considerable portion of the nitrogen appearing in the flue gases may come from the gaseous fuel.

The composition of dry air may ordinarily be taken as constant, containing 21.0 per cent oxygen and 79.0 per cent nitrogen by volume, the nitrogen content including the argon present. Under certain conditions the air used in combustion may contain appreciable amounts of carbon dioxide, making a separate gas analysis of the air valuable. The moisture content of air is subject to extreme variations depending upon weather conditions so that a separate determination of the moisture content of air is invariably necessary. This is easily obtained by measuring its dew-point or the depression of the wet-bulb thermometer.

Because of the constancy of composition of dry air it is possible to calculate readily the weight of air used in a combustion process from a knowledge of the nitrogen content of the gaseous products and of the fuel used. Accordingly, the general rule is expressed that the *weight of dry air actually used in complete or partial combustion processes is calculated from a nitrogen balance.*

The oxygen balance might also be employed for calculating the weight of air actually used, but this basis is more uncertain. In the first place, the oxygen content of air is only one-fourth as much as the nitrogen content. Second, oxygen enters into many states of combination whereas nitrogen remains entirely inert. For example, oxygen may come from the oxygen in the moisture of the air or fuel, or from combined water in the fuel. In the gaseous products it appears as oxygen, carbon monoxide, carbon dioxide, sulphur dioxide, and water vapor, and in the ashes as ferric oxide or other oxides. If the coal burned contains pyrites, oxygen will appear in the ashes as iron oxide and in the gases as sulphur dioxide. If calcium sulphate were present in the coal it might be reduced to produce carbon dioxide in the flue gases.

The chief objection to the use of the nitrogen balance basis is that in

250 WEIGHT AND HEAT BALANCES OF COMBUSTION PROCESSES

gas analysis, errors due to unabsorbed components accumulate on the nitrogen determination which is always found by difference.

Nitrogen Balance. Basis: 100 lb coal fired.

Nitrogen in gaseous products =	36.90 lb-mols
Nitrogen from coal = $1.30/28.0 =$	0.0464 lb-mol
Nitrogen from air =	36.85 lb-mols
Dry air supplied = $36.85/0.79 =$	46.6 lb-mols
or $46.6 \times 29 =$	1354 lb

It will be noted that the nitrogen content of the coal might be neglected without introducing a serious error.

4. Weight of Moisture in Air.

The weight of moisture per mol of dry air depends upon the temperature, pressure, and relative humidity of the air. From the dew-point the partial pressure of the water vapor is determined, and the moisture content of the air may be calculated by the methods explained in Chapter IV. If the wet-bulb temperature of the air is measured the humidity may be determined directly from the humidity chart. Although this chart is strictly applicable only when the total pressure is 760 millimeters of mercury, it may ordinarily be used for any process conducted at atmospheric pressure.

Dry-bulb temperature =	73.0° F
Wet-bulb temperature =	59.4° F
From Fig. 10, the molal humidity of the air is 0.012	
Water supplied with air = $46.6 \times 0.012 =$	0.559 lb-mol

5. Total Volume of Wet Air Introduced.

Basis: 100 lb coal fired.

Total mols of moist air = $46.6 + 0.559 =$	47.2 lb-mols
Volume at 73° F, 29.08 in. Hg =	
$47.2 \times 359 \times \frac{29.92}{29.08} \times \frac{533}{492} =$	18,870 cu ft

6. Weight of Moisture in Gaseous Products.

To complete the weight balance it is necessary to know the weight of moisture in the gaseous products since this is not obtained by the ordinary gas analysis. Direct measurement of the moisture content is difficult. Wet-bulb temperature measurements of hot flue gases are apt to be in serious error because of radiation. The water content can be determined directly by absorption in concentrated sulphuric or in dry calcium chloride or it can be calculated from a measurement of the dew-point. It can also be calculated if the composition of the dry flue gases, the moisture content of the air used, and the hydrogen and moisture in the fuel burned are known. As a general rule it may be stated

that the *moisture content of the gaseous products is calculated from a hydrogen balance.*

Hydrogen Balance. Basis: 100 lb coal fired.

Input

From moisture introduced with dry air =	0.559 lb-mol
From combined water in coal = $6.31/18$ =	0.351 lb-mol
From free moisture in coal = $4.38/18$ =	0.244 lb-mol
From available hydrogen in coal = $3.50/2.016$ =	1.738 lb-mols
Total	2.892 lb-mols

Output

The Orsat apparatus used for analyzing the stack gases does not determine hydrocarbon gases. However, in an efficiently operated boiler furnace, the hydrocarbons are present only in small quantities. It will therefore be assumed that all the hydrogen introduced into the system leaves as water in the stack gases.

Hydrogen in H_2O of stack gases = 2.892 lb-mols

The dew-point of the stack gases may now be determined.

Partial pressure of H_2O = $\frac{2.892}{45.1 + 2.892} \times 739 = 44.5$ mm Hg.

From Fig. 6, this partial pressure is seen to correspond to a dew-point of $36^\circ C$ or $97^\circ F$.

7. Total Volume of Gaseous Products.

Basis: 100 lb coal fired.

Mols of wet gas = $45.1 + 2.892$ = 48.0 lb-mols

Volume at $488^\circ F$ and 29.08 in. Hg =

$48.0 \times 359 \times \frac{29.92}{50.00} \times \frac{948}{14.7} =$ 34,150 cu ft

Summary of Weight Balances. To verify the accuracy of experimental data or methods of calculation a summary of all weight balances is prepared: The total, overall weight balance is also indicated on the flow-chart of Fig. 42.

TOTAL WEIGHT BALANCE

<i>Input</i>		<i>Output</i>	
Coal	100 lb	Refuse	21.2 lb
Dry air (46.6 lb-mols)	1354 lb	Dry gases (45.1 lb-mols)	1367 lb
H_2O in air (0.559 lb-mol) ..	10.05 lb	H_2O in stack gases (2.892 lb-mols)	52.1 lb
Total	1464 lb	Total	1440 lb

CARBON BALANCE

In coal	65.93 lb	In gases	63.26 lb
		In refuse	2.67 lb
Total	65.93 lb		65.93 lb

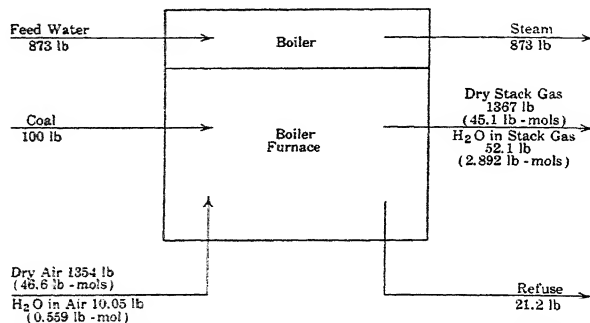


Fig. 42. Weight Balance of Steam Generating Plant. (Illustration 1.)

NITROGEN BALANCE

In air (36.85 lb-mols).....	1040 lb	In stack gases	
In coal.....	1.30 lb	(36.90 lb-mols).....	1041 lb
Total.....	1041 lb	Total.....	1041 lb

HYDROGEN BALANCE

In water vapor of air		In H ₂ O of stack gases	
(0.559 lb-mol).....	1.127 lb	(2.892 lb-mols).....	5.83 lb
In combined water of coal			
(0.351 lb-mol).....	0.708 lb		
In free moisture of coal			
(0.244 lb-mol).....	0.491 lb		
Available hydrogen of coal			
(1.738 lb-mols).....	3.50 lb		
Total.....	5.83 lb	Total.....	5.83 lb

ASH BALANCE

In coal.....	18.58 lb	In refuse.....	18.58 lb
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OXYGEN BALANCE

In combined water of coal		In CO ₂ of stack gases	
$6.31 \times 16/18$	5.61 lb	5.26×32	168.5 lb
In free moisture of coal		In O ₂ of stack gases	
$4.38 \times 16/18$	3.89 lb	2.94×32	94.2 lb
In dry air		In CO of stack gases	
$36.85 \times 21/79 \times 32$	313.5 lb	$0.01804/2 \times 32$	0.289 lb
In water vapor in air		In H ₂ O of stack gases	
$0.559/2 \times 32$	8.95 lb	$2.892/2 \times 32$	46.3 lb
Total.....	332 lb	Total.....	309 lb

It will be seen that there is a deficit of 24 lb or 1.6 per cent on the output side of the total weight balance. This discrepancy falls entirely on the oxygen balance since no direct calculations were made from the oxygen basis. The oxygen content of the fuel is obtained by difference, so that all errors in any other determination of the coal analysis will accumulate algebraically upon this value. In this particular case the deficit of 24 pounds in the total weight balance indicates that the content of the carbon in the coal, or the content of the carbon monoxide or carbon dioxide in the gas, is low.

Other errors or omissions in chemical analysis will be reflected in the weight balance. For example, the oxygen content of the air supply might be less than 21.0 per cent, and some carbon dioxide might enter with the air and would escape consideration unless a special analysis of the air were made. The presence of any suspended tar or soot in the gaseous products might introduce a very serious error in the entire weight balance. Despite the many sources of error in weight balances calculated from chemical analysis, this method still remains as accurate as the direct measurement of gas volumes by the methods ordinarily available.

8. Theoretical Amount of Air Required for Combustion.

The weight of air theoretically required for complete combustion depends entirely upon the chemical composition of the fuel and the stoichiometric relations involved in combustion. Since the one element in common for all combustion reactions is oxygen, it is obvious that the *weight of air required for combustion must be calculated from an oxygen balance*, each atom of carbon requiring one mol of oxygen and each mol of hydrogen requiring one-half mol of oxygen. The oxygen already in the fuel is assumed to be in combination with hydrogen, hence only the available hydrogen of the fuel is considered in calculating its oxygen requirement.

Per Cent Excess Air

Basis: 100 lb coal fired.

OXYGEN BALANCE

Oxygen requirements for combustible constituents of coal charged.

	Oxygen Required
Carbon 65.93 lb = 5.49 lb-atoms	5.49 lb-mols
Net hydrogen 3.50 lb = 1.736 lb-mols	0.868 lb-mol
Total	6.358 lb-mols
Air required = $6.358/0.21 =$	30.3 lb-mols
Air supplied =	46.6 lb-mols
Excess air = $46.6 - 30.3 =$	16.3 lb-mols
Per cent excess air = $16.3/30.3 \times 100 =$	53.9%

HEAT BALANCE

In developing the heat balance for the boiler furnace, Equation (10) of Chapter VII will be utilized.

$$Q_S + H_R = H_P + Q$$

The standard heat of reaction, Q_S , equals the heat of combustion of the fuel, minus the heats of combustion of the refuse and stack gases.

Since it is conventional to utilize total rather than net heating values in heat balances of this type, the reference state for all water involved in the process will be the liquid state; the heat contents of reactants and products are evaluated on that basis. In the above equation Q represents the heat absorbed by the steam generated plus the undetermined losses.

The various detailed items that constitute the complete heat balance are as follows:

Heat Input Items (left side of equation).

1. Heating value of coal.
2. Heat content of the coal.
3. Heat content of the dry air.
4. Heat content of the water vapor accompanying the dry air.

Heat Output Items (right side of equation).

1. Heating value of refuse.
2. Heating value of stack gases.
3. Heat content of refuse.
4. Heat content of the dry stack gases.
5. Heat content of the water vapor in stack gases.
6. Heat utilized in generating steam.
7. Undetermined losses.

Reference temperature: 65° F.

Basis: 100 lb coal fired.

Input

1. Heating value of the coal = $100 \times 11,670 =$	1,167,000 Btu
2. Heat content of the coal =	0 Btu
3. Heat content of the dry air = $46.6 \times 6.93 \times (73-65) =$	2,580 Btu
4. Heat content of the water vapor accompanying the dry air. Dew-point of the air from Fig. 9 = 49° F Latent heat of vaporization = 19,140 Btu per lb-mol Heat content = $0.559[8.35(73-49) + 19,140 - 18(65-49)] =$	10,660 Btu
Total heat input.	1,180,240 Btu

Output

1. Heating value of refuse. Weight of carbon in refuse = 2.67 lb Heating value = $2.67 \times 14,550 =$	38,850 Btu
2. Heating value of stack gases. Lb-mols of CO in stack gases = 0.01804 lb-mol Heating value = $0.01804 \times 67,620 \times 1.8 =$	2,200 Btu

3. Heat content of refuse.

Weight of refuse = 21.2 lb

Heat content = $21.2 \times 0.23 \times (255-65) = \dots\dots\dots$ 1,090 Btu

4. Heat content of the dry stack gases.

Mean heat capacities between 65 and 488° F taken from

Fig. 14, page 117.

Heat content of $\text{CO}_2 = 5.26 \times 9.70 \times$
(488 - 65) = $\dots\dots\dots$ 21,600 BtuHeat content of $\text{CO} + \text{O}_2 + \text{N}_2 =$ $39.86 \times 7.03 \times (488 - 65) = \dots\dots\dots$ 118,600 BtuTotal $\dots\dots\dots$ 140,200 Btu

5. Heat content of the water vapor in stack gases.

Dew-point of stack gases = 36° C or 97° F

Latent heat of vaporization (Fig. 9) =

18,660 Btu per lb-mol

Heat of the liquid = $2.892 \times 18 \times (97-65) = \dots\dots\dots$ 1,665 BtuLatent heat of vaporization = $2.892 \times 18,660 = \dots\dots\dots$ 53,900 BtuSuperheat = $2.892 \times 8.49 \times (488-97) = \dots\dots\dots$ 9,600 BtuTotal heat content $\dots\dots\dots$ 65,200 Btu

6. Heat utilized in generating steam.

Pounds steam generated = $\frac{1,038,400}{119,000} \times 100 = 873$ lbHeat content of 1 lb steam as pro-
duced (151.7 lb per sq in. abso-
lute, 1.7% moisture), relative
to 32° F = $331.4 + 862.3 - (0.017 \times 862.3) = \dots\dots\dots$ 1179.0 Btu per lbHeat content of feed water at 193° F relative to 32° F = $\dots\dots\dots$ 160.9 Btu per lb

Net heat input into steam produced = 1018.1 Btu per lb

Total heat absorbed by steam produced =

 $873 \times 1018.1 = \dots\dots\dots$ 890,000 Btu7. Undetermined losses (by difference) = $\dots\dots\dots$ 42,700 Btu

Summarized Heat Balance of Steam Generating Plant:

Reference temperature: 65° F

Basis: 100 lb coal fired.

	Heat Input	
	Btu	Per cent
1. Heating value of the coal $\dots\dots\dots$	1,167,000	98.9
2. Heat content of the coal $\dots\dots\dots$	0	0
3. Heat content of the dry air $\dots\dots\dots$	2,580	0.2
4. Heat content of the water vapor accompanying the dry air $\dots\dots\dots$	10,660	0.9
Total $\dots\dots\dots$	1,180,240	100.0

Heat Output

1. Heating value of refuse	38,850	3.3
2. Heating value of stack gases	2,200	0.2
3. Heat content of refuse	1,090	0.1
4. Heat content of the dry stack gases	140,200	11.9
5. Heat content of the water vapor in the stack gases	65,200	5.5
6. Heat utilized in generating steam	890,000	75.4
7. Undetermined losses (by difference)	42,700	3.6
Total	1,180,240	100.0

This heat balance is summarized in Fig. 43.

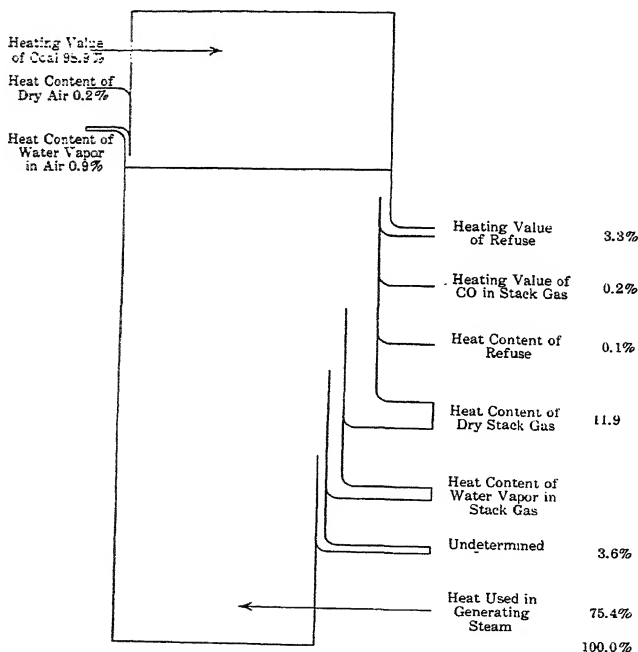


FIG. 43. Heat Balance of Steam Generating Plant. (Illustration 1.)

Thermal Efficiency and Economy. The thermal efficiency of a boiler furnace may be calculated on the total or the net heating value of the coal. The effectively utilized heat is that which is absorbed in steam generation.

Based on total heating value of coal,

the thermal efficiency is $\frac{890,000}{1,167,000}$ or 76.3%

Based on net heating value of coal,

the thermal efficiency is $\frac{890,000}{1,167,000 - (42)(1060)}$ or 78.2%

The low percentage of undetermined heat losses, 3.6%, indicates that the furnace is well insulated. The heat lost in the refuse as unburned carbon can be reduced below 1% by improved stokers. The stack losses can be reduced by increasing the length of travel of gases across the boiler tubes so that gases will enter the stack at a lower temperature. This latter economy will require improved design and possibly use of forced draft.

Case 2. Combustion Calculations Where Ultimate Analysis of Coal is Not Completely Known. In the preceding illustration, the calculations were completed without making any assumptions as to the composition of the fuel. However, the determination of the hydrogen content of coal is a difficult procedure, to be avoided if possible. For this reason it is sometimes desirable to calculate the weight balance of a furnace or gas producer without data on hydrogen content and to calculate this quantity from an oxygen balance. In this illustration an additional complication is introduced in that some of the coal drops through the grate without coking.

Where the hydrogen content of the fuel is calculated from an oxygen balance great care must be taken in analyzing the flue gases. The sampling and determination of oxygen in hot flue gases are particularly uncertain. For this reason it is frequently preferable to estimate the hydrogen content of the fuel by empirical methods such as those illustrated on page 213 for coal, page 222 for gases, and Fig. 38, page 218 for oils. The calculations are then carried out as in the preceding illustration.

In the preceding illustration the nitrogen content of the coal was known. In making a complete ultimate analysis it is necessary to determine this element in order that the oxygen content may be obtained by difference. However, from the results of the previous illustration it is apparent that the nitrogen in the coal might be neglected altogether, assuming all nitrogen in the flue gases to have come from the air. No appreciable error will result from neglecting this nitrogen except in determining the oxygen or combined water content of the coal by difference. For this calculation it is ordinarily sufficient to assume a nitrogen content of 1.7 per cent of the combustible in the coal. This assumption will ordinarily not be in error by more than 0.3 per cent of the weight of

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the combustible except in the case of anthracite coals. Greater refinement is not justified because of the uncertainty of the sampling of the coal and of other data on which the weight balance is based.

Illustration 2. Coal-Fired Boiler Furnace. A furnace is fired with a bituminous coal having the following proximate analysis:

Moisture.....	2.9%
Volatile matter.....	33.8%
Fixed carbon.....	53.1%
Ash.....	10.2%
	<hr/>
	100.0%

The ultimate analysis is known only in part and includes (as-received basis):

Sulphur.....	1.1%
Carbon.....	73.8%

The dry refuse from the furnace has the following composition:

Volatile matter.....	3.1%
Fixed carbon.....	18.0%
Ash.....	78.9%
	<hr/>
	100.0%

The Orsat analysis of the flue gases is as follows:

Carbon dioxide.....	12.1%
Carbon monoxide.....	0.2%
Oxygen.....	7.2%
Nitrogen.....	80.5%
	<hr/>
	100.0%

Air enters the furnace at a temperature of 65° F with a percentage humidity of 55%. The barometric pressure is 29.30 in. of Hg. The flue gases enter the stack at a pressure equivalent to 1.5 in. of water less than the barometric pressure and at a temperature of 560° F.

Water is fed to the boiler at a temperature of 60° F and vaporized to form wet steam at a gauge pressure of 100 lb per sq in., quality 98%, at a rate of 790 lb of steam or water per 100 lb of coal charged.

Compute complete weight and heat balances, the volumes of air and flue gases per 100 lb of coal charged, and the percentage excess air used.

WEIGHT BALANCE

Calculations are made similarly to Illustration 1 with special methods in parts 1, 4, 5.

1. Total carbon content of refuse.

Basis: 100 lb of coal charged.

The weight of refuse is calculated from the ash contents of the coal and of the refuse. The weight of ash in 100 lb of coal is 10.2 lb. This weight of ash constitutes but 78.9% of the weight of refuse.

$$\text{Total weight of refuse} = \frac{10.2}{0.789} = \dots\dots\dots 12.9 \text{ lb}$$

Carbon exists in the refuse as fixed carbon and as volatile matter. The volatile matter is due to the dropping of uncoked coal through the grate. The combustible of the uncoked coal in the refuse may be assumed to have the same composition as the combustible of the coal fired. Therefore, the ratio of combustible to volatile matter in the uncoked coal in the refuse will be the same as that in the coal.

Ratio of combustible matter to volatile matter in the coal

$$= \frac{33.8 + 53.1}{33.8} = \dots\dots\dots 2.56$$

$$\text{Volatile matter in refuse} = 12.9 \times 0.031 = \dots\dots\dots 0.40 \text{ lb}$$

$$\text{Unchanged combustible in refuse} = 0.40 \times 2.56 = \dots\dots\dots 1.02 \text{ lb}$$

Carbon is also present in the refuse as coked coal accompanied by no volatile matter. The amount of carbon as coke is the difference between quantities of total combustible and of unchanged coal combustible in the refuse.

$$\text{Fixed carbon in refuse} = 12.9 \times 0.18 = \dots\dots\dots 2.32 \text{ lb}$$

$$\text{Total combustible in refuse} = 2.32 + 0.40 = \dots\dots\dots 2.72 \text{ lb}$$

$$\text{Coked combustible (carbon)} = 2.72 - 1.02 = \dots\dots\dots 1.70 \text{ lb}$$

The total carbon content of the unchanged combustible in the refuse may be determined from the percentage of carbon in the combustible of the original coal.

$$\text{Total carbon content of combustible of coal} = \frac{73.8}{33.8 + 53.1} = \dots\dots\dots 85\%$$

$$\text{Carbon in uncoked coal in refuse} = (0.85) (1.02) = \dots\dots\dots 0.87 \text{ lb}$$

$$\text{Total carbon in refuse} = 1.70 + 0.87 = \dots\dots\dots 2.57 \text{ lb}$$

2. Weight of dry flue gases.

Carbon Balance. Basis: 100 lb of coal charged.

$$\text{Carbon gasified} = 73.8 - 2.57 = 71.2 \text{ lb or} \dots\dots\dots 5.94 \text{ lb-atom}$$

1.0 lb-mol of dry flue gases contains:

$$\text{Carbon dioxide} \dots\dots\dots 0.121 \text{ lb-mol}$$

$$\text{Carbon monoxide} \dots\dots\dots 0.002 \text{ lb-mol}$$

$$\text{Total carbon per pound-mol of gas} = \dots\dots\dots 0.123 \text{ lb-atom}$$

$$\text{Total dry flue gas} = \frac{5.94}{0.123} = \dots\dots\dots 48.3 \text{ lb-mols}$$

Total dry gases:

$$\text{CO}_2 = 48.3 \times 0.121 = 5.85 \text{ lb-mols or } \times 44 = \dots\dots\dots 258 \text{ lb}$$

$$\text{CO} = 48.3 \times 0.002 = 0.096 \text{ lb-mol or } \times 28 = \dots\dots\dots 3 \text{ lb}$$

$$\text{O}_2 = 48.3 \times 0.072 = 3.48 \text{ lb-mols or } \times 32 = \dots\dots\dots 111 \text{ lb}$$

$$\text{N}_2 = 48.3 \times 0.805 = 38.87 \text{ lb-mols or } \times 28.2 = \dots\dots\dots 1097 \text{ lb}$$

$$\text{Total} = \dots\dots\dots 48.30 \text{ lb-mols or } \dots\dots\dots 1469 \text{ lb}$$

3. Weight of air supplied.

Nitrogen Balance. Basis: 100 lb of coal charged.

$$\text{N}_2 \text{ in flue gases} = \dots\dots\dots 38.87 \text{ lb-mols}$$

Assuming all N₂ to come from the air:

$$\text{Dry air supplied} = \frac{38.87}{0.79} = \dots\dots\dots 49.2 \text{ lb-mols}$$

$$\text{or } 49.2 \times 29 = \dots\dots\dots 1430 \text{ lb}$$

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From Fig. 9:

Molal humidity of air =	0.012	
Water vapor in air =	$0.012 \times 49.2 =$	0.59 lb-mol
or	$0.59 \times 18 =$	10.6 lb
Total wet air =	$49.2 + 0.59 =$	49.8 lb-mols
or	$1430 + 10.6 =$	1440 lb
Volume of air entering at 65° F, 29.3 in. of Hg =		
	$49.8 \times 359 \times \frac{525}{492} \times \frac{29.92}{29.30} =$	19,450 cu ft

4. Hydrogen content of coal.

Oxygen Balance. Basis: 100 lb of coal charged.

$$\text{Oxygen in dry flue gas} = 5.85 + \frac{0.096}{2} + 3.48 = 9.38 \text{ lb-mols}$$

$$\text{Oxygen entering in dry air} = 49.2 \times 0.21 = 10.32 \text{ lb-mols}$$

Assuming that the oxygen not accounted for in the dry flue gases was consumed in oxidizing the available hydrogen of the coal:

$$\text{O}_2 \text{ oxidizing H}_2 = 10.32 - 9.38 = 0.94 \text{ lb-mol}$$

$$\text{H}_2 \text{ burned} = 2 \times 0.94 = 1.88 \text{ lb-mols or } 3.79 \text{ lb}$$

The hydrogen burned may be taken as the available hydrogen of the coal, neglecting the small hydrogen content of the uncoked combustible in the refuse.

5. Complete ultimate analysis of coal. The unknown items of the ultimate analysis are combined water and nitrogen. As pointed out on page 257, the nitrogen content may be assumed to be $1.7 \times 0.87 = 1.4\%$. The combined water may then be determined as the difference between 100 and the sum of the percentages of moisture, carbon, hydrogen, sulphur, nitrogen, and corrected ash.

$$\begin{aligned} \text{Corrected ash} &= 10.2 - 3/8(1.1) = 9.8\% \\ \text{Combined H}_2\text{O} &= 100 - (2.9 + 73.8 + 3.8 + 1.1 + 1.4 + 9.8) = 7.2\% \end{aligned}$$

Ultimate analysis:

Moisture.....	2.9%
Carbon.....	73.8%
Available H ₂	3.8%
Sulphur.....	1.1%
Nitrogen.....	1.4%
Corrected ash.....	9.8%
Combined H ₂ O.....	7.2%
	<hr/>
	100.0%

6. Water vapor in flue gases.

Hydrogen Balance. Basis: 100 lb of coal charged.

$$\text{H}_2\text{O from air} = 0.59 \text{ lb-mol}$$

$$\text{H}_2\text{O from coal} = \frac{2.9 + 7.2}{18} = 0.56 \text{ lb-mol}$$

$$\text{H}_2\text{O formed from H}_2 = 1.88 \text{ lb-mols}$$

$$\text{Total} = 3.03 \text{ lb-mols or } 55 \text{ lb}$$

7. Volume of wet flue gases.

$$\begin{aligned}
 \text{Mols of wet flue gas} &= 48.3 + 3.03 = \dots\dots\dots 51.33 \text{ lb-mols} \\
 \text{Pressure in flue} &= 29.30 - \frac{1.5}{13.6} \dots\dots\dots 29.19 \text{ in. of Hg} \\
 \text{Volume at } 560^\circ \text{ F, } 29.19 \text{ in. of Hg} \\
 51.33 \times 359 \times \frac{492}{492} \times \frac{29.92}{29.19} &= \dots\dots\dots 39,200 \text{ cu ft}
 \end{aligned}$$

8. Complete weight balance.

Input

Coal.....	100 lb
Dry air (49.2 lb-mols).....	1430 lb
Water vapor in air (0.59 lb-mol).....	10 lb
Total.....	1540 lb

Output

Dry flue gases (48.3 lb-mols).....	1469 lb
Refuse.....	13 lb
Water vapor in flue gas (3.03 lb-mols).....	55 lb
Total.....	1537 lb

This weight balance is summarized in Fig. 44.

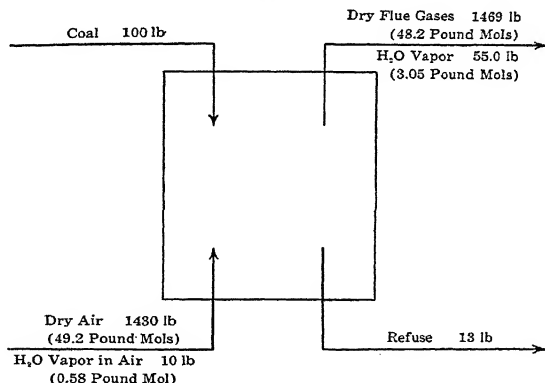


Fig. 44 Weight Balance of a Boiler Furnace. (Illustration 2.)

Percentage excess air.

100 lb of coal charged.

$$\begin{aligned}
 \text{Total carbon in coal charged} &= 73.8 \text{ lb} = \dots\dots\dots 6.15 \text{ lb-mols} \\
 \text{Available hydrogen in coal charged} &= \dots\dots\dots 1.88 \text{ lb-mols} \\
 \text{Total O}_2 \text{ required} &= \frac{1.88}{2} + 6.15 = \dots\dots\dots 7.09 \text{ lb-mols} \\
 \text{Air theoretically required} &= \frac{7.09}{0.21} = \dots\dots\dots 33.8 \text{ lb-mols} \\
 \text{Air actually supplied} &= \dots\dots\dots 49.2 \text{ lb-mols}
 \end{aligned}$$

Percentage excess air = $\frac{49.2 - 33.8}{33.8} = 45.5\%$, based on that required for complete combustion of all carbon and available hydrogen in the coal charged and neglecting that required for sulphur.

The percentage excess air may also be calculated directly from the flue-gas analysis:

Basis: 100 lb-mols of flue gas.

Neglecting N_2 from the coal:

$$O_2 \text{ introduced in air} = \frac{80.5}{0.79} \times 0.21 = \dots\dots\dots 21.4 \text{ lb-mols}$$

$$O_2 \text{ in excess} = (\text{surplus present in gases minus that required to complete oxidation of the CO}) =$$

$$7.2 - \frac{0.2}{2} = \dots\dots\dots 7.1 \text{ lb-mols}$$

$$O_2 \text{ actually consumed} = \dots\dots\dots 14.3 \text{ lb-mols}$$

$$\text{Percentage excess oxygen} = \text{percentage excess air} = \frac{7.1}{14.3} = 49.6.$$

This percentage excess is based on the oxygen required for all combustible substances which were *actually burned*.

HEAT BALANCE

The heat balance of this problem is calculated exactly as in Illustration 1, estimating the heating value of the coal by the empirical method discussed on page 213.

Effect of Sulphur in Coal. In the preceding illustrations the combustion of the sulphur in the coal has been neglected. This does not introduce appreciable error if the sulphur content is low, 1.0 per cent or less. It is difficult to take into account the combustion of the sulphur by any rigorous method because of the uncertainty of the forms in which it is present in the coal and the difficulty of determining its distribution in the combustion products. A considerable part of the sulphur which is present in the coal in a combustible or available form will appear as sulphur dioxide in the flue gases. The remainder will be present in the refuse.

The ordinary scheme of flue gas analysis by the Orsat apparatus, in which the gas sample is confined over water, does not permit determination of sulphur dioxide. Because of the high solubility of sulphur dioxide in water (about thirty times that of carbon dioxide) the bulk of the SO_2 will be absorbed in the water of the sampling apparatus and burette. Any SO_2 which is not removed in this manner will be absorbed and reported as CO_2 . The reported analysis will ordinarily represent approximately the composition of the SO_2 -free gases. Methods are available by which separate determination may be made of the SO_2 , but this is not ordinarily feasible for performance tests of combustion equipment.

Neglect of the combustion of sulphur in calculations of the type car-

ried out in Illustration 1, in which the oxygen balance is not used, does not introduce any serious error, even if the sulphur content is relatively high. The calculated total weight of dry flue gases will be low by approximately the weight of SO_2 formed. This error is usually negligible. However, in the method of calculation of Illustration 2, in which the net hydrogen in the coal is calculated from an oxygen balance, the errors resulting from neglect of combustion of sulphur may be more serious. In this type of calculation it is assumed that all free oxygen not accounted for as CO_2 , CO , or free oxygen in the flue gas was utilized in the oxidation of the net hydrogen of the coal. This assumption neglects the oxygen consumed in oxidation of sulphur. As a result the net hydrogen content calculated by this method will be too high, and the combined water content, calculated by difference, will be too low. These errors are particularly high when the sulphur is originally present as iron pyrites, FeS_2 , in which case oxygen is consumed in the oxidation of both the sulphur and the iron. However, because of the relatively high atomic weight of sulphur it is permissible to neglect these errors in dealing with coals containing less than 1 per cent of sulphur.

The probable errors involved in neglecting the combustion of the sulphur may be estimated for a typical case by consideration of the data of Illustration 2. The coal contained 1.1 per cent sulphur. The maximum error would result if all the sulphur were in the form of iron pyrites. In this case, for each pound-atom of sulphur present $11/8$ pound-mols of oxygen would be consumed in producing SO_2 and Fe_2O_3 . On the basis of 100 pounds of coal charged 0.048 pound-mol of oxygen would be required for combustion of the sulphur of the coal. Introducing this value into the oxygen balance on page 260 will reduce the unaccounted-for oxygen, used in oxidizing hydrogen, from 0.94 to 0.89 pound-mol. The calculated net hydrogen is correspondingly reduced from 3.8 to 3.6 pounds and the combined water content is increased from 7.2 to 7.4 pounds. These errors are not serious and in addition represent maximum errors because actually not all the sulphur will be in the pyritic form and furthermore it will not be completely burned.

Case 3. Method of Calculation Where Sulphur is High and the Carbon and Hydrogen Contents of the Coal are Unknown. Where sulphur contents of more than about 1 per cent are encountered it is not ordinarily desirable to use the oxygen balance for computing the net hydrogen content of the coal. In order to develop an accurate oxygen balance it would be necessary to have data on the forms in which the sulphur occurred in the coal and on the sulphur content of the refuse. Without such data the net hydrogen content is better determined analytically or estimated by the empirical method of Uehling, discussed

on page 213. This latter method may also be used to estimate the total carbon in the coal from a determination of the heating value.

If the sulphur content of a coal is so high that sulphur dioxide constitutes a considerable part of the flue gas it is necessary to obtain data from which the amount of sulphur actually burned may be calculated. A determination of either the sulphur in the refuse or of the SO_2 in the flue gases will supply this information. The former determination is more easily carried out. It may then be assumed that the ordinary flue gas analysis yields the composition of the SO_2 -free gases and the total quantity of gases computed on this basis. Direct determination of the SO_2 content of the flue gases is more reliable but frequently unwarranted.

In calculating a heat balance involving a coal of high sulphur content a sulphur correction should be applied to the heating value directly determined in the oxygen bomb calorimeter. This correction results from the fact that in the calorimeter the available sulphur is burned almost entirely to SO_3 whereas in ordinary combustion the major part of it will form SO_2 . The correction may be taken as 1000 calories per gram of sulphur, to be subtracted from the observed heating value.

Case 4. Gas Producers. In the operation of a gas producer, a fuel gas of low calorific value is produced by blowing air, usually accompanied by steam, through a deep incandescent bed of fuel. Carbon monoxide and carbon dioxide are formed by partial combustion of the fuel. Hydrogen and the oxides of carbon are formed from the reduction of water, and volatile combustible matter is distilled from the coal without combustion.

The weight balance of a gas producer is represented by the following items:

Input

1. Weight of fuel charged.
2. Weight of dry air supplied.
3. Weight of moisture in air supplied.
4. Weight of steam supplied.

Output

1. Weight of dry gaseous products.
2. Weight of water vapor in gaseous products.
3. Weight of tar and soot suspended in gas.
4. Weight of tar deposited in flues.
5. Weight of refuse.

Effect of Soot and Tar. In many combustion processes and particularly in those involving the distillation of fuels as in coke ovens or in the partial combustion of fuels as in gas producers the gaseous products contain carbon suspended in the form of soot and tar. These forms of

carbon will not appear in an ordinary volumetric gas analysis but must be determined separately by absorption or retention on a weighed filter. The tar can then be separated and analyzed for its hydrogen content although this precision is not usually warranted. It is ordinarily sufficient to assume that the combustible of the suspended tar analyzes 90 per cent carbon and 10 per cent hydrogen and that the combustible of the soot consists of 100 per cent carbon. Frequently ashes will also appear suspended in the gaseous products so that the ash content of the suspended material should also be measured.

In addition to the tar and soot suspended in the gases a gradual accumulation of these products will settle in the flues. The slight correction necessary for this is usually made by measuring the deposition over a long period of time, for example, over the usual time interval elapsed between successive cleanings of the flues. The tar deposit is removed and weighed and, the tons of fuel distilled over the known time interval being known, a rough approximation can be obtained for the carbon deposited per kilogram of coal charged.

Method of Calculation Where Steam is Introduced and Where Soot and Tar are Not Negligible. The following illustration is of value in that consideration is given to the tar and soot suspended in the producer gas and also to the live steam which is passed into the producer. The problem is of added interest in that all experimental data were collected with unusual care. Analyses of gas and coal and measurements of temperatures were made at regular intervals over several days of operation and data carefully weighted to give average results. These data were taken in part from a report by C. B. Harrop.¹

Illustration 3. Air is supplied to a gas producer at 75° F with a percentage humidity of 75% and a barometric pressure of 29.75 in. of Hg. Coal weighing 70,900 lb and having a gross heating value of 11,910 Btu per lb is charged into the producer. Tar weighing 591 lb is deposited in the flues prior to the point of gas sampling and contains 93% carbon and 7% hydrogen.

The water vapor, suspended tar, and soot in the gases were determined experimentally by withdrawing samples of the gas through an absorption train. The results are expressed in grains per cubic foot of wet, hot gas measured at 1075° F and 29.75 in. of Hg.

Water vapor.....	3.43 grains per cu ft
Suspended tar.....	3.31 grains per cu ft
Suspended soot.....	1.52 grains per cu ft

It is assumed that the suspended tar is 90% carbon and 10% hydrogen and that the soot is 100% carbon.

Saturated steam at a gauge pressure of 25.3 lb per sq in. is introduced at the bottom of the fuel bed.

¹ Jour. Am. Ceramic Soc. 1, 35 (1918).

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Analysis of coal as charged:

Carbon.....	66.31%	Nitrogen...	1.52%	Sulphur.....	1.44%
Available hydrogen.	3.53%	Total water.	23.16%	Corrected ash	4.04%
					Total..... 100.00%
Ash (as weighed).....					4.58%

Analysis of refuse:

Moisture.....	1.10%	Fixed carbon	3.08%	Ash.....	95.82%
					Total..... 100.00%

Analysis of dry, tar- and soot-free gas, by volume:

CO ₂	7.12%	CO.....	21.85%	H ₂	13.65%
O ₂	0.90%	CH ₄	3.25%	N ₂	53.24%
					Total..... 100.00%

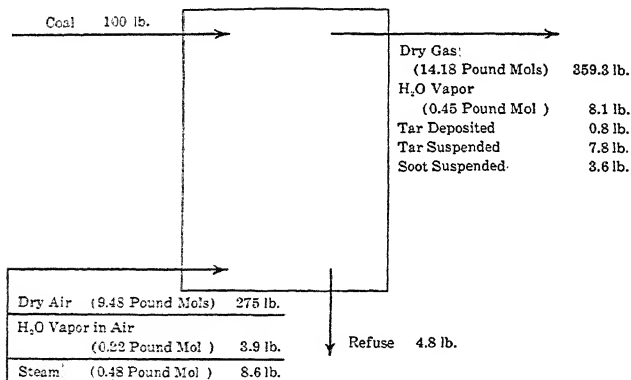


FIG. 45. Weight Balance of a Gas Producer. (Illustration 3.)

The gases leave the flue at 1075° F and 29.75 in. of Hg. The refuse leaves the producer at 350° F and may be assumed to have a specific heat of 0.22. The mean specific heat of the tar and soot between 75° F and 1075° F may be assumed to be 0.32. The heating value of the suspended tar was found to be 16,000 Btu per lb, and that of the deposited tar 15,500 Btu per lb.

Calculate a complete weight and material balance for the operation of this gas producer.

Solution: Since a majority of the details of this problem are similar to those of Illustration 1, full explanations of all steps will not be repeated. A flow-chart of this process is shown in Fig. 45.

WEIGHT BALANCE

Special attention should be given to calculations shown in Parts 1 and 3.

1. Weight of gaseous products.

Carbon Balance:

Carbon gasified: *Basis:* 100 lb of coal charged.

Carbon in coal = $100 \times 0.6631 = \dots\dots\dots$ 66.31 lb or 5.526 lb-atoms

Carbon in deposited tar = $\frac{591}{709} \times 0.93 = \dots\dots\dots$ 0.78 lb or 0.065 lb-atom

Weight of refuse = $4.58/0.9582 = \dots\dots\dots$ 4.79 lb

(calculated on the basis of the ash as weighed in the proximate analysis).

Carbon in refuse = $4.79 \times 0.0308 = \dots\dots\dots$ 0.148 lb or 0.012 lb-atom

Carbon gasified = $5.526 - (0.065 + 0.012) = \dots\dots\dots$ 5.449 lb-atoms

Carbon in clean gases. *Basis:* 1.0 mol of dry, tar- and soot-free gas.

C in $\text{CO}_2 = \dots\dots\dots$ 0.0712 lb-atom

C in CO = $\dots\dots\dots$ 0.2185 lb-atom

C in $\text{CH}_4 = \dots\dots\dots$ 0.0325 lb-atom

Total = $\dots\dots\dots$ 0.3222 lb-atom

Water, tar and soot in gas. *Basis:* 1000 cu ft of wet gases at 1075°F and 29.75 in. of Hg.

Mols of total gas = $\frac{1000}{359 \times \frac{1535}{492} \times \frac{29.92}{29.75}} = \dots\dots\dots$ 0.888 lb-mol

H_2O present = $\frac{3.43 \times 1000}{7000 \times 18} = \dots\dots\dots$ 0.0272 lb-mol

Mols dry gas = $\dots\dots\dots$ 0.8608 lb-mol

Water per mol of dry gas $0.0272/0.8608 = \dots\dots\dots$ 0.0316 lb-mol

Tar per mol of dry gas $\frac{3.31 \times 1000}{7000 \times 0.8608} = \dots\dots\dots$ 0.550 lb

Soot per mol of dry gas $\frac{1.52 \times 1000}{7000 \times 0.8608} = \dots\dots\dots$ 0.252 lb

Total carbon in gases. *Basis:* 1.0 lb-mol of dry, clean gas.

C in clean gases = $\dots\dots\dots$ 0.3222 lb-atom

C in tar = $0.550 \times 0.9 = 0.495$ lb or $\dots\dots\dots$ 0.0412 lb-atom

C in soot = 0.252 lb or $\dots\dots\dots$ 0.0210 lb-atom

Total. $\dots\dots\dots$ 0.3844 lb-atom

Mols of dry gas per 100 lb of coal = $5.449/0.3844 = 14.18$ lb-mols.

Total products in gases. *Basis:* 100 lb of coal charged.

$\text{CO}_2 = 14.18 \times 0.0712 = 1.01$ lb-mols or $\times 44 = \dots\dots\dots$ 44.5 lb

$\text{O}_2 = 14.18 \times 0.0090 = 0.12$ lb-mol or $\times 32 = \dots\dots\dots$ 3.8 lb

CO = $14.18 \times 0.2185 = 3.10$ lb-mols or $\times 28 = \dots\dots\dots$ 86.8 lb

$\text{CH}_4 = 14.18 \times 0.0325 = 0.46$ lb-mol or $\times 16 = \dots\dots\dots$ 7.4 lb

$\text{H}_2 = 14.18 \times 0.1365 = 1.94$ lb-mols or $\times 2 = \dots\dots\dots$ 3.8 lb

$\text{N}_2 = 14.18 \times 0.5324 = 7.55$ lb-mols or $\times 28.2 = \dots\dots\dots$ 213.0 lb

Total dry, clean gas 14.18 lb-mols or $\dots\dots\dots$ 359.3 lb

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Water

$$14.18 \times 0.0316 = 0.45 \text{ lb-mol, or } \times 18 = \dots\dots\dots 8.1 \text{ lb}$$

Tar

$$C = 14.18 \times 0.0412 = 0.58 \text{ lb-atom, or } \times 12 = 7.02 \text{ lb}$$

$$H_2 = 14.18 \times 0.055/2 = 0.39 \text{ lb-mol, or } \times 2 = \underline{0.78 \text{ lb}}$$

$$\text{Total tar} = \dots\dots\dots 7.80 \text{ lb}$$

Soot

$$C = 14.18 \times 0.0210 = 0.30 \text{ lb-atom, or } \times 12 = \dots\dots\dots \underline{3.6 \text{ lb}}$$

$$\text{Total products in gases} = \dots\dots\dots \underline{378.8 \text{ lb}}$$

2. Weight of air supplied.

Nitrogen Balance. Basis: 100 lb of coal charged.

$$N_2 \text{ in gas} = \dots\dots\dots 7.55 \text{ lb-mols}$$

$$N_2 \text{ in coal} = 1.52/28 = \dots\dots\dots \underline{0.05 \text{ lb-mol}}$$

$$N_2 \text{ from air} = \dots\dots\dots 7.50 \text{ lb-mols}$$

$$\text{Dry air supplied} = 7.50/0.79 = \dots\dots\dots 9.48 \text{ lb-mols}$$

$$\text{or } 9.48 \times 29.0 = \dots\dots\dots 275 \text{ lb}$$

$$\text{Molal humidity of air (Fig. 9)} = \dots\dots\dots 0.023$$

$$\text{Water in air} = 9.48 \times 0.023 = \dots\dots\dots 0.218 \text{ lb-mol}$$

$$\text{or } 0.218 \times 18 = \dots\dots\dots 3.9 \text{ lb}$$

$$\text{Total wet air} = 0.218 + 9.48 = \dots\dots\dots 9.70 \text{ lb-mols}$$

$$\text{or } 275 + 3.9 = \dots\dots\dots 278.9 \text{ lb}$$

3. Weight of steam introduced.

Hydrogen Balance. Basis: 100 lb of coal charged.

Output

$$H_2 \text{ in deposited tar} = \frac{591}{709} \times 0.07 = 0.0585 \text{ lb} = \dots\dots\dots 0.029 \text{ lb-mol}$$

$$\text{Free } H_2 \text{ in gas} = \dots\dots\dots 1.94 \text{ lb-mol}$$

$$H_2 \text{ in } CH_4 \text{ in gas} = 0.46 \times 2 = \dots\dots\dots 0.92 \text{ lb-mol}$$

$$H_2 \text{ in } H_2O \text{ in gas} = \dots\dots\dots 0.45 \text{ lb-mol}$$

$$H_2 \text{ in suspended tar} = \dots\dots\dots \underline{0.39 \text{ lb-mol}}$$

$$\text{Total output of } H_2 = \dots\dots\dots 3.73 \text{ lb-mols}$$

Input

$$\text{Net } H_2 \text{ in coal} = 3.53/2.02 = \dots\dots\dots 1.75 \text{ lb-mols}$$

$$H_2 \text{ in water in coal} = 23.16/18 = \dots\dots\dots 1.28 \text{ lb-mols}$$

$$H_2 \text{ in water in air} = \dots\dots\dots \underline{0.22 \text{ lb-mol}}$$

$$\text{Total input in addition to steam} = \dots\dots\dots 3.25 \text{ lb-mols}$$

$$H_2 \text{ from steam} = 3.73 - 3.25 = \dots\dots\dots \underline{0.48 \text{ lb-mol}}$$

$$\text{Steam introduced} = 0.48 \text{ lb-mol or } \dots\dots\dots 8.64 \text{ lb}$$

4. Total weight balance.

<i>Input</i>		<i>Output</i>	
Coal.....	100 lb	Refuse.....	4.8 lb
Dry air (9.48 lb-mols)....	275 lb	Tar deposited.....	0.83 lb
Water in air (0.22 lb-mol) .	3.9 lb	Soot suspended.....	3.6 lb
Steam (0.48 lb-mol).....	8.6 lb	Tar suspended.....	7.8 lb
		Dry clean gas (14.18 lb-mols)	359.3 lb
Total.....	387.5 lb	Water in gas (0.45 lb-mols)...	8.1 lb
		Total.....	384.43 lb

The slight discrepancy in the totals of the weight balance results from inaccuracies of the data and neglect of the sulphur content of the coal. The weight balance is also summarized in Fig. 45.

5. Gaseous volumes. *Basis:* 100 lb of coal charged.

$$\text{Volume of wet air} = 9.70 \times 359 \times \frac{535}{492} \times \frac{29.92}{29.75} = \dots\dots\dots 3,800 \text{ cu ft}$$

$$\text{Volume of wet gases} = 14.63 \times 359 \times \frac{1535}{492} \times \frac{29.92}{29.75} = \dots\dots\dots 16,500 \text{ cu ft}$$

HEAT BALANCE

Special attention is called to calculations in Parts 2, 3 and 5 of output.

Reference temperature: 75° F.

Basis: 100 lb of coal charged.

Input

1. Heating value of coal = $100 \times 11,910 = \dots\dots\dots 1,191,000 \text{ Btu}$

2. Sensible heat of coal = $\dots\dots\dots 0 \text{ Btu}$

3. Heat content of steam:

Pressure = $25.3 + 14.7 = 40.0 \text{ lb per sq in.}$

From Table IX, page 143, the total heat content referred to 32° F is seen to be 1171 Btu per lb.

Referred to 75° F this becomes $1171 - 43 = 1128 \text{ Btu per lb}$

Heat content of steam = $8.6 \times 1128 = \dots\dots\dots 9,700 \text{ Btu}$

4. Heat content of dry air = $\dots\dots\dots 0 \text{ Btu}$

5. Total heat content of water vapor in air.

Dew-point (Fig. 10) = 66° F

Heat content (as in Illustration 1, page 254) = $\dots\dots\dots 4,100 \text{ Btu}$

Total = $\dots\dots\dots 1,204,800 \text{ Btu}$

Output

1. Heating value of dry clean producer gas. (Calculated from composition)..... 794,000 Btu

2. Heating value of suspended tar = $7.80 \times 16,000 = \dots\dots\dots 125,000 \text{ Btu}$

3. Heating value of soot = $0.30 \times 97,000 \times 1.8 = \dots\dots\dots 52,400 \text{ Btu}$

4. Heating value of carbon in refuse = $0.012 \times 97,000 \times 1.8 = \dots\dots\dots 2,100 \text{ Btu}$

5. Heating value of deposited tar = $0.83 \times 15,500 = \dots\dots\dots 12,900 \text{ Btu}$

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6. Heat content of dry, clean producer gas.

Mean heat capacity between 75° F and 1075° F, calculated from the data of Fig. 14. Total $C_{pm}(75 - 1075^\circ \text{F}) = 108.0$

Heat content = $108.0 (1075 - 75) = \dots\dots\dots$ 108,000 Btu

7. Sensible heat content of tar and soot.

Suspended tar and soot = $11.4 \times 0.32 (1075 - 75) = \dots\dots\dots$ 3,650 Btu

Deposited tar and soot = $0.8 \times 32 (1075 - 75) = \dots\dots\dots$ 250 Btu

8. Total heat content of water vapor in gases.

Total molal heat content calculated by method used in

Illustration 1 = $\dots\dots\dots$ 27,400 Btu

Total heat content = $27,400 \times 0.45 = \dots\dots\dots$ 12,300 Btu

9. Sensible heat content of refuse = 0.22×4.8

$(350 - 75) = \dots\dots\dots$ 300 Btu

Total heat accounted for = $\dots\dots\dots$ 1,110,900 Btu

10. Heat losses, radiation, etc. = $1,204,800 - 1,110,900 = \dots\dots\dots$ 93,900 Btu

Summary of Heat Balance:

Reference temperature: 75° F.

Basis: 100 lb of coal charged.

<i>Input</i>		
1. Heating value of coal.....	1,191,000 Btu	98.9%
2. Sensible heat of coal.....	0 Btu	0%
3. Sensible heat in air.....	0 Btu	0%
4. Heat content of steam.....	9,700 Btu	0.8%
5. Total heat content of water in air.....	4,100 Btu	0.3%
Total.....	1,204,800 Btu	100.0%

<i>Output</i>		
1. Heating value of clean gas.....	794,000 Btu	66.0%
2. Heating value of suspended tar.....	125,000 Btu	10.4%
3. Heating value of suspended soot.....	52,400 Btu	4.3%
4. Heating value of carbon in refuse.....	2,100 Btu	0.2%
5. Heating value of deposited tar.....	12,900 Btu	1.0%
6. Heat content of dry, clean gas.....	108,000 Btu	8.9%
7. Heat content of tar and soot.....	3,900 Btu	0.3%
8. Heat content of water vapor in gases.....	12,300 Btu	1.0%
9. Heat content of refuse.....	300 Btu	0.0%
10. Heat losses, radiation, etc.....	93,900 Btu	7.9%
Total.....	1,204,800 Btu	100.0%

This heat balance is presented in diagrammatic form in Fig. 46.

THERMAL EFFICIENCIES

Cold gas. The effectively utilized heat includes only the heating value of the dry, clean gas.

$$\text{Efficiency} = \frac{\text{---}}{\text{---}}$$

Hot gas. The effectively utilized heat includes the total sensible heat of all materials in the gases and also the heating value of the suspended tar and soot.

Sensible heat of dry, clean gases =	108,000 Btu
Sensible heat of water vapor in gases = $12,300 - (0.45 \times 18,900) =$	3,800 Btu
Sensible heat of suspended tar and soot =	3,650 Btu
Heating value of dry, clean gas =	794,000 Btu
Heating value of tar and soot =	177,400 Btu
Effectively utilized heat =	1,086,850 Btu

$$\text{Efficiency} = \frac{1,086,850}{1,204,800} = 90.0\%$$

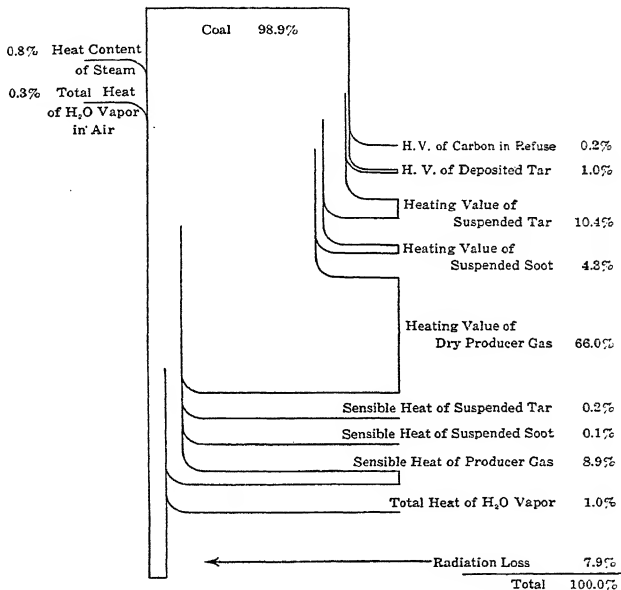


FIG. 46. Heat Balance of a Gas Producer. (Illustration 3.)

The principal loss in the operation of this particular gas producer is by radiation and conduction of heat from the apparatus. This loss could be minimized by further insulation, but insulation alone might prove unsatisfactory. Further insulation would result in a higher temperature of the gaseous products and a higher temperature of operation. Excessive temperatures are to be avoided since this hastens the destruction of the refractory lining of the producer by abrasion and slugging action. Furthermore, increased temperature would increase the amount of clinker by fusion of the ash. To avoid clinkering at high temperatures it would be necessary

to use a high-grade fuel. In order to economize on heat loss by insulation and at the same time operate at lower temperature to avoid clinker formation and refractory losses it is customary practice to introduce steam into the base of the gas producer. This lowers the temperature and transforms part of the chemical energy of the coal into hydrogen, carbon monoxide, and carbon dioxide resulting from the reaction of steam with coke. The chief objection to the introduction of steam is that the carbon dioxide content of the gases is increased and some water vapor passes through without decomposition, thus lowering the heating value of the gaseous products per unit volume. The chief advantages in the use of steam are that it permits the use of a low-grade fuel, and better thermal insulation.

Case 5. Combustion of a Gaseous Fuel in an Intermittent Process.

To illustrate the methods of solving problems arising in the combustion of gaseous fuels complete weight and heat balances will be developed for a gas-fired ceramic kiln. The general method of calculating the heat balance of a gas-fired furnace is the same as that used in dealing with coal-fired equipment. The weight of dry gaseous products is best computed from a carbon balance, the weight of air from a nitrogen balance, and the weight of water from a hydrogen balance, exactly as in the preceding illustrations.

The illustration selected is of particular interest in that it deals with the combustion of a hot producer gas carrying tar and soot in suspension which is used for heating an intermittent ceramic kiln used for burning common brick. The bricks, after thorough air drying, are stacked in the cold kiln. The producer gas is burned in several port openings distributed at equal distances about the base of the kiln. The burning gases rise through internal vertical flues, and then descend in direct contact with the bricks, finally passing to a chimney. All gases given off by the bricks are mixed with the flue gases and discharged with them.

The operating conditions of such a kiln vary continuously throughout a run. At the start, with the kiln and charge cold, the firing is begun gradually and the flue gases leave the kiln at practically atmospheric temperature. As the charge of bricks is warmed the temperature of the flue gas rises, the rate of firing is increased, and water vapor is evolved from the ware and mixes with the flue gases. The heat and weight balances of such a process are best based on a complete cycle of operation. The total quantity of fuel burned during the entire cycle is measured and its average composition determined by frequent analyses. From frequent measurements of the temperatures and compositions of the air and flue gases throughout the entire cycle average values are obtained.

The water removed from the brick is evolved in two distinct stages. At a temperature of about 125° C the mechanically entrained and loosely adsorbed water is removed. In order to evaporate this water the heat

of "unwetting" of the clay must be supplied as well as the heat of normal vaporization. At a temperature of about 560° C the molecules of the clay undergo decomposition and water of chemical constitution is evolved. Since these evolutions of water vapor from the brick occur only during the early stages of heating, called the "water-smoking" period, it is convenient to consider each as a separate stream of products, even though both are discharged in admixture with the flue gases. Thus it may be considered that three streams of gaseous products leave the kiln: (1) The flue gases proper, having a more or less constant saturation temperature or dew-point; (2) the vapor formed by the evaporation of mechanically entrained water in the bricks which is considered as discharged at the average temperature of the flue gases during the period of its evolution; (3) the vapor formed by the evolution of chemically combined water from the bricks which is considered as discharged at the average temperature of the flue gases during the period of its evolution. The saturation temperatures of the water vapor of items 2 and 3 may be taken as the saturation temperatures of the flue gases during their respective periods of evolution.

After the water of chemical constitution is removed from the bricks, further heating produces vitrification and other changes which are accompanied by small thermal effects. The magnitudes of these effects are unknown and they are left unaccounted for in the heat balance. The data in the following illustration are taken in part from the work of C. B. Harrop.¹

Illustration 4. Weight Balance of a Gas-Fired, Intermittent Ceramic Kiln. An intermittent brick kiln is heated by burning producer gas of the following composition by volume on the dry, clean basis:

CO ₂	7.12%
CO.....	21.85%
CH ₄	3.25%
O ₂	0.09%
H ₂	13.65%
N ₂	54.04%
	<hr/> 100.00%

Each kilogram-mol of the dry, clean producer gas carries with it 0.544 kg of tar (90% carbon and 10% hydrogen), 0.251 kg of soot (100% carbon), and 0.0316 kg-mol of water vapor. The heating value of the tar is found to be 8890 Calories per kg. The specific heat of the tar and soot may be assumed to be 0.31.

The producer gas enters the burners at an average temperature of 580° C and is burned with air at an average temperature of 24° C, a percentage humidity of 75%, and a pressure of 756 mm Hg. The average composition by volume of the resulting flue gases is as follows, on the moisture-free basis:

¹ J. Am. Cer. Soc. 1, 35 (1918).

CO ₂	10.49%
O ₂	6.18%
CO.....	0.12%
CH ₄	0.10%
H ₂	0.66%
N ₂	82.45%
	<hr/> 100.00%

The average temperature, over the entire cycle of operation, at which the flue gases leave the kiln is 345° C. The average barometric pressure is 756 mm of Hg.

The damp bricks charged into the kiln at atmospheric temperature contained 0.543% mechanically entrained water or moisture on the basis of the damp weight. On firing, the brick clay undergoes a further loss in weight of 3.39%, on the moisture-free basis, assumed to represent chemically combined water. During the period of removal of the mechanically entrained water the flue gases leave the kiln saturated with water vapor at an average temperature of 60° C. During the removal of the chemically combined water the gases leave the kiln at an average temperature of 150° C with a dew-point of 60° C.

At the end of the run the average temperatures and weights of the charge and kiln structure are as follows:

Baked ware (bricks).....	175,042 kg	1118° C
Crown of kiln.....	49,432 kg	477° C
Side wall of kiln.....	45,562 kg	429° C
Hob of kiln.....	45,017 kg	423° C

The mean specific heats of all the above materials may be assumed to be 0.23.

During the entire burning cycle 4552 kg-mols of dry, clean producer gas are burned.

In the endothermic reactions of breaking down the chemical structure of the clay of the bricks and liberating the chemically combined water it is found that 261 calories are absorbed in the liberation of 1 gram of water in the liquid state.

- Compute a weight balance of the combustion of the producer gas based on 100 kg-mols of dry, clean producer gas burned, and calculate the percentage excess air used.
- Calculate a complete heat balance of the entire unit based on the entire cycle of operation.

WEIGHT BALANCE OF COMBUSTION PROCESS ONLY

Basis: 100 kg-mols of dry, clean producer gas.

1. Total producer gas burned.

Dry, clean gas:

CO ₂ = 7.12 kg-mols or ×44 =	313 kg
CO = 21.85 kg-mols or ×28 =	611 kg
CH ₄ = 3.25 kg-mols or ×16 =	52 kg
O ₂ = 0.09 kg-mols or ×32 =	3 kg
H ₂ = 13.65 kg-mols or ×2.02 =	28 kg
N ₂ = 54.04 kg-mols or ×28.2 =	1525 kg
<hr/> 100.00 kg-mols or	<hr/> 2532 kg

Water vapor 3.16 kg-mols or $\times 18 = \dots\dots\dots$ 57 kg
 Suspended soot (carbon) = $\dots\dots\dots$ 25.1 kg
 Suspended tar

Hydrogen 5.44 kg

Carbon 48.96 kg

Total 54.40 kg = $\dots\dots\dots$ 54.4 kg

Total weight = $\dots\dots\dots$ 2668 kg

Molal humidity = 0.0316

Dew-point (Fig. 9, page 96) = 24° C

2. Weight of dry flue gases.

Carbon Balance.

Output

Basis: 100 kg-mols of dry flue gases.

C in $\text{CO}_2 = \dots\dots\dots$ 10.49 kg-atoms

C in CO = $\dots\dots\dots$ 0.12 kg-atom

C in $\text{CH}_4 = \dots\dots\dots$ 0.10 kg-atom

Total = $\dots\dots\dots$ 10.71 kg-atoms

Input

Basis: 100 kg-mols of dry, clean producer gas.

C in $\text{CO}_2 = \dots\dots\dots$ 7.12 kg-atoms

C in CO = $\dots\dots\dots$ 21.85 kg-atoms

C in $\text{CH}_4 = \dots\dots\dots$ 3.25 kg-atoms

C in suspended soot = $25.1/12 = \dots\dots\dots$ 2.09 kg-atoms

C in suspended tar = $49/12 = \dots\dots\dots$ 4.08 kg-atoms

Total = $\dots\dots\dots$ 38.39 kg-atoms

Mols of flue gas formed $\frac{38.39}{10.71} \times 100 = \dots\dots\dots$ 358 kg-mols

Total dry flue gas:

$\text{CO}_2 = 0.1049 \times 358 = 37.5$ kg-mols or $\times 44 = \dots\dots\dots$ 1650 kg

$\text{O}_2 = 0.0618 \times 358 = 22.1$ kg-mols or $\times 32 = \dots\dots\dots$ 707 kg

CO = $0.0012 \times 358 = 0.43$ kg-mol or $\times 28 = \dots\dots\dots$ 12 kg

$\text{CH}_4 = 0.0010 \times 358 = 0.36$ kg-mol or $\times 16 = \dots\dots\dots$ 5.8 kg

$\text{H}_2 = 0.0066 \times 358 = 2.36$ kg-mols or $\times 2 = \dots\dots\dots$ 4.7 kg

$0.8245 \times 358 = 295.2$ kg-mols or $\times 28.2 \dots\dots\dots$ 8320 kg

Total = $\dots\dots\dots$ 358 kg-mols or $\dots\dots\dots$ 10,700 kg

3. Weight of air introduced.

Nitrogen Balance: *Basis:* 100 kg-mols of dry, clean producer gas.

N_2 in flue gas = $0.8245 \times 358 = \dots\dots\dots$ 295 kg-mols

N_2 in producer gas = $\dots\dots\dots$ 54 kg-mols

N_2 from air = $\dots\dots\dots$ 241 kg-mols

Dry air introduced = $\frac{241}{0.79} = \dots\dots\dots$ 305 kg-mols

or $305 \times 29.0 = \dots\dots\dots$ 8850 kg

276 WEIGHT AND HEAT BALANCES OF COMBUSTION PROCESSES

Molal humidity of air (Fig. 10) =	0.0225
Water introduced = 0.0225×305 =	6.8 kg-mols
or 6.8×18 =	122 kg
Wet air introduced = $305 + 6.8$ =	311.8 kg-mols

4. Water vapor in flue gases.

Hydrogen Balance. Basis: 100 kg-mols of dry, clean producer gas.

Input

Producer gas:

H_2 in CH_4 = 3.25×2 =	6.50 kg-mols
H_2 as H_2 =	13.65 kg-mols
H_2 in H_2O =	3.16 kg-mols
H_2 in water vapor in air =	6.85 kg-mols
H_2 in tar = $5.44/2.02$ =	2.70 kg-mols
Total input =	32.86 kg-mols

Output

In dry flue gas:

H_2 in CH_4 = $0.0010 \times 358 \times 2$ =	0.72 kg-mol
H_2 as H_2 = 0.0066×358 =	2.36 kg-mols
Accounted for =	3.08 kg-mols

In water vapor of flue gas =

$32.86 - 3.08$ =	29.78 kg-mols
------------------------	---------------

Total output =	32.86 kg-mols
----------------------	---------------

Water vapor in flue gas =

or 29.78×18 =	536 kg
Total wet flue gases = $358 + 29.78$ =	388 kg-mols
or $10,700 + 536$ =	11,236 kg

5. Percentage excess air used.

Basis: 100 kg-mols of dry, clean producer gas.

Combustible Component

O₂ required

Clean gas:

CO = 21.85 kg-mols	$21.85/2$	= ..	10.93 kg-mols
CH ₄ = 3.25 kg-mols	3.25×2	= ..	6.50 kg-mols
H ₂ = 13.65 kg-mols	$13.65/2$	= ..	6.83 kg-mols

Tar:

H_2 = 2.70 kg-mols	$2.70/2$	=	1.35 kg-mols
C = 4.07 kg-atoms		=	4.07 kg-atoms

Soot:

C = 2.09 kg-atoms	=	2.09 kg-atoms
Total O ₂ required	=	31.77 kg-mols

Oxygen present in gas =

O ₂ required from air =	0.09 kg-mol
	31.68 kg-mols

Air theoretically required	$\frac{31.68}{0.210}$	151.0 kg-mols
Percentage excess :	$\frac{305 - 151}{151}$	102%

6. Summary of weight balance of combustion of producer gas.

Basis: 100 kg-mols of dry, clean producer gas.

<i>Input</i>	
Dry, clean producer gas (100 kg-mols) =	2532.0 kg
Suspended tar =	54.4 kg
Suspended soot =	25.1 kg
Water vapor in producer gas (3.16 kg-mols) =	57.0 kg
Dry air (305 kg-mols) =	8850.0 kg
Water vapor in air (6.8 kg-mols) =	122.0 kg
Total input =	11,640.5 kg
<i>Output</i>	
Dry flue gas (358 kg-mols) =	10,700 kg
Water in flue gas (29.78 kg-mols) =	536 kg
Total output =	11,236 kg

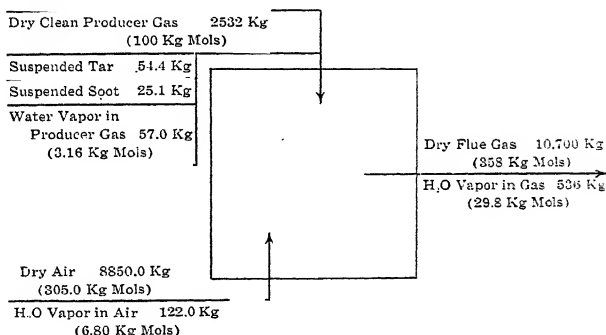


FIG. 47. Weight Balance of a Gas-Fired Kiln. (Illustration 4.)

This weight balance is summarized diagrammatically in Fig. 47. The discrepancy between the input and output of the balance results from inaccuracies in analytical data which would cause errors in the oxygen balance with this method of calculation.

HEAT BALANCE OF ENTIRE PROCESS

The heat balance of this entire process may be calculated in the usual manner. Special items to be considered are the heating values of the tar and soot in the gas and of the deposited tar, the heat required to remove the mechanical and chemical water from the charge, and the heat left in the charge and structure at the end of the run. This balance is summarized in Fig. 48.

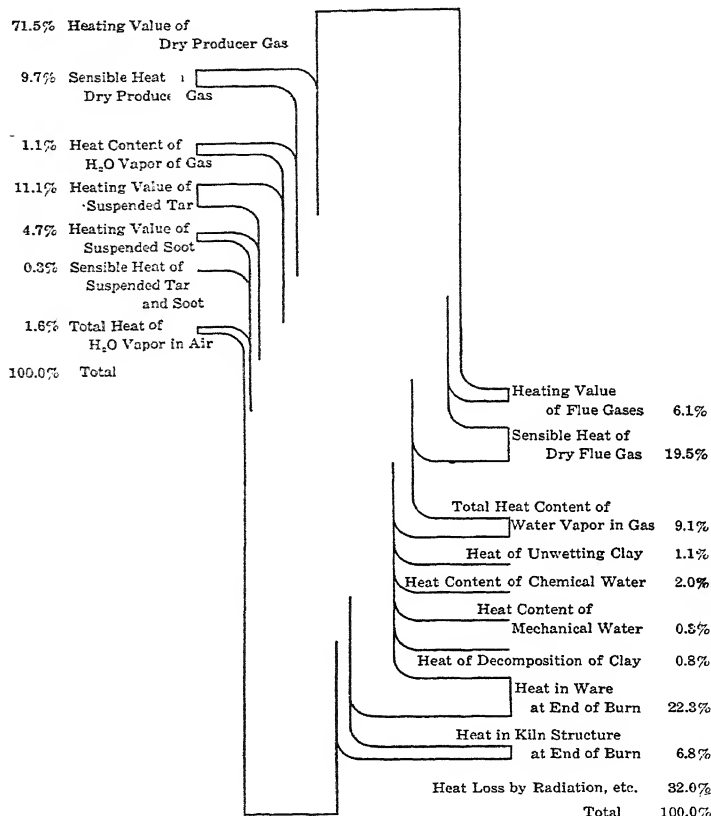


FIG. 48. Heat Balance of a Gas-Fired Kiln. (Illustration 4.)

GRAPHICAL CALCULATION OF COMBUSTION PROBLEMS

Where short-cut methods of combustion calculations are desired a simple graphical solution may be resorted to provided that the following items are negligible: sulphur content of fuel, combustible content of refuse, water vapor in air, suspended tar and soot in gases, and hydrocarbons in flue gases. The simplified graphical solution of such combustion problems appears in Fig. 48a. This method also serves as an approximate solution for other combustion problems where the experi-

mental data or time required do not warrant precise methods. From Fig. 48a there may be obtained directly the pounds of air used and the pound-mols of wet flue gas produced and the carbon dioxide content of the dry flue gas on the basis of 1 pound of combustible in oil, coal, or

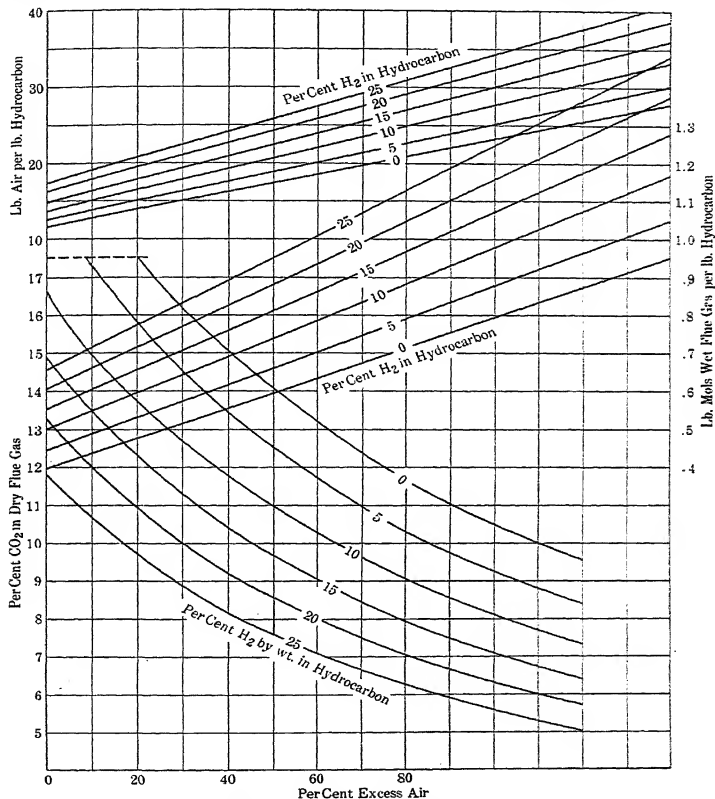


FIG. 48a. Combustion Chart for Fuels.

coke for variations in percentage excess air used for combustion and for variations in the available hydrogen content of the combustible. Heat balances can then be built with additional data on the temperature of the flue gases and by calculating all heating values and heat contents by methods previously described in this chapter.

PROBLEMS

1. A Pennsylvania bituminous coal has the following composition:

H ₂	4.71%
C.....	69.80%
N ₂	1.42%
O ₂	7.83%
Ash.....	6.73%
H ₂ O.....	9.51%
Total heating value.....	6950 Calories per kg

This coal is gasified in a gas producer using air at 20° C saturated with water vapor. No additional steam or water is admitted into the producer. The barometric pressure is 740 mm. The resulting gas has the following composition:

H ₂	0.5%
CO.....	21.2%
N ₂	64.5%
CH ₄	5.8%
CO ₂	6.2%
O ₂	1.8%

It may be assumed that no tar or soot is present in the producer gas. During a test period the total coal charged is 10,500 kg.

The dry refuse formed weighs 825 kg and contains 13.3% C.

Temperature of refuse = 220° C.

Mean specific heat of refuse = 0.25.

Temperature of outgoing gases = 450° C.

- Calculate complete weight and heat balances of this gas producer on the basis of 100 kg of coal as charged.
- Calculate the thermal efficiency on both the hot and cold bases.
- Calculate the total volume of gases leaving the producer.
- Calculate the heating value of the producer gas in Btu per cubic foot measured at 60° F, 30 in. of Hg, saturated with water vapor.

2. A gas producer is charged with bituminous coal having the following composition:

Proximate analysis:

Moisture.....	2.70%
Volatile matter.....	25.77%
Fixed carbon.....	62.87%
Ash.....	8.66%

100.00%

Ultimate analysis:

Moisture.....	2.70%
Carbon.....	78.55%
Net hydrogen.....	4.13%
Nitrogen.....	1.58%
Sulphur.....	0.69%
Corrected ash.....	8.40%
Combined H ₂ O.....	3.95%

100.00%

Total heating value = 13,944 Btu per lb.

Air is supplied at 75° F with a percentage humidity of 90%. The barometric pressure is 29.65 in. of Hg. Dry, saturated steam is supplied at a gauge pressure of 50 lb per sq in. The producer gas leaves at a temperature of 1220° F and has the following composition by volume:

CO.....	25.0%
H ₂	22.0%
CH ₄	3.6%
C ₂ H ₄	2.8%
CO ₂	9.2%
N ₂	37.4%
	<hr/> 100.0%

A sample of gas is withdrawn and cooled to 100° F for determination of suspended tar and soot. The tar and soot content is 10 grains per cu ft of gas measured at barometric pressure, 100° F, and saturated with water vapor. The tar and soot contain 95% carbon and 5% hydrogen. Its heating value is 17,100 Btu per lb, and its mean specific heat is 0.34. The dew-point of the producer gas is 100° F.

The refuse is discharged at 400° F, moisture-free, and containing 4.52% carbon. The specific heat of the refuse is assumed to be 0.23. The mean molal heat capacity of C₂H₄ (75° to 1220° F) is 20 Btu per lb-mol per °F.

Neglecting deposition of tar in the flues and presence of sulphur, calculate:

- Complete heat and weight balances of the producer, based on 100 lb of coal charged.
- The thermal efficiencies on both the hot and cold bases.
- The volume of producer gas, measured at 60° F, 30 in. of Hg, saturated with water formed per 100 lb of coal charged.
- The heating value of the producer gas, per standard cubic foot.

The solution of this problem results in a negative radiation loss. What errors in experimental data are most likely responsible for this condition?

3. An Illinois bituminous coal is burned in a boiler furnace with air at 78° F, 92% percentage humidity. The barometric pressure is 29.40 in. of Hg. The furnace gases leave at 553° F. The refuse is discharged moisture-free, at 440° F. The refuse as analyzed contains 12.2% carbon as coke and 16.1% moisture. The specific heat of the dry refuse is 0.25. The proximate analysis of coal is:

Fixed carbon.....	50.34%
Volatile matter.....	30.68%
Moisture.....	9.61%
Ash.....	9.37%

Heating value of coal = 11,900 Btu per lb.

The ultimate analysis on the moisture-free basis is:

Carbon.....	73.70%
Hydrogen.....	4.75%
Oxygen.....	9.23%
Nitrogen.....	1.58%
Sulphur.....	0.55%
Corrected ash.....	10.19%
	<hr/> 100.00%

282 WEIGHT AND HEAT BALANCES OF COMBUSTION PROCESSES

The flue gas analysis is as follows:

CO ₂	12.2%
CO.....	0.2%
O ₂	7.0%
N ₂	80.6%
	<hr/>
	100.0%

Calculate:

- Total weight and heat balances for this process based on 100 lb of coal charged, neglecting the combustion of sulphur. The heat losses and the heat effectively utilized may be considered together as a single item of heat output.
 - Percentage excess air used in combustion, based on that required for complete combustion of all coal charged.
 - The dew-point of the flue gases.
 - The actual volumes in cubic feet at the given condition of temperature, humidity and pressure of the flue gases and air supply, per 100 lb of coal charged.
4. A bituminous coal is burned in a boiler furnace with air at 85° F, 90% percentage humidity. The barometric pressure is 29.20 in. of Hg. The furnace gases leave at 572° F. The refuse leaves the furnace moisture-free at 520° F and when analyzed contains 22.3% moisture, 12.3% volatile matter and 41.1% fixed carbon. The mean specific heat of the refuse is 0.23. The proximate analysis of the coal is:

Fixed carbon.....	56.34%
Volatile matter.....	37.75%
Moisture.....	2.97%
Ash.....	2.94%

A partial ultimate analysis on the corrected ash- and moisture-free basis is:

Carbon.....	84.43%
Nitrogen.....	2.00%
Sulphur.....	0.82%

The total heating value of the coal is 14,139 Btu per lb. Dry, saturated steam weighing 780 lb at a gauge pressure of 150 lb per sq in. is produced per 100 lb of coal charged. Water is fed into the boiler at 72° F. The Orsat analysis of the flue gas is:

CO ₂	12.0%
CO.....	1.2%
O ₂	6.2%
N ₂	80.6%

Calculate:

- The net hydrogen content of the coal from an oxygen balance, neglecting combustion of sulphur.
- The complete ultimate analysis of the coal.
- The complete weight balance of the process, based on 100 lb of coal charged.
- The complete heat balance of the furnace, based on 100 lb of coal charged.
- The thermal efficiencies of the furnace and boiler, based on the total and on the net heating values.
- The percentage excess air used, based on the total combustible charged.

5. A heat interchanger, used for heating the oil in a circulating hot oil heating system, is fired with coal having the following proximate analysis:

Moisture.....	12.38%
Volatile matter.....	36.88%
Fixed carbon.....	37.50%
Ash.....	13.24%
	<hr/>
	100.00%

The heating value of the coal is 10,361 Btu per lb, and its sulphur content is 5.1%.

The coal is burned with air at a temperature of 70° F and a percentage humidity of 60%. The barometric pressure is 29.3 in. of Hg.

The refuse from the furnace is discharged at a temperature of 600° F and contains 16% fixed carbon and 84% ash. The sulphur content of the refuse is 7.8%. Its specific heat may be taken as 0.23.

The flue gases leave the furnace at a temperature of 850° F and have the following composition by volume, on the sulphur- and moisture-free basis.

CO ₂	11.50%
CO.....	0.17%
O ₂	7.51%
N ₂	80.82%
	<hr/>
	100.00%

The oil is circulated at a rate of 3800 lb per 100 lb of coal charged and is heated from 155° F to 464° F. The mean specific heat of the oil in this temperature range is 0.55. Calculate:

- The complete ultimate analysis of the coal as estimated from the rank and heating value.
- The complete weight and heat balances of the interchanger, based on 100 lb of coal charged.
- The complete analysis, by volume, of the wet flue gases leaving the interchanger.
- The percentage excess air, based on the combustible actually burned.
- The volume of wet flue gases leaving the interchanger.
- The thermal efficiencies of the interchanger, based on both the total and net heating values.

6. A brick kiln, of the type described in Illustration 4, is fired with 10,420 lb-mols of dry producer gas. The weight of green ware is 410,000 lb containing 0.52% mechanical water and 3.02% chemically combined water. The gas enters the kiln at 1220° F and a pressure of 29.65 in. of Hg, and contains 10 grains of tar (90% C, 10% H) per cu ft measured at a pressure of 29.65 in. of Hg, 100° F, and saturated with water vapor. The dew-point of the producer gas is 100° F.

During the water-smoking period mechanical water is vaporized and leaves the kiln at 300° F, and the chemically combined water leaves at 400° F. During water-smoking the saturation temperature of the gases is 150° F. The flue gas leaves at an average temperature of 720° F. The average temperature of the ware at the end of the burn is 2100° F, and its specific heat is 0.23. The producer gas is burned with air at 75° F, 90% percentage humidity, and a pressure of 29.65 in. of Hg. Average analysis of gases by volume on the moisture-free basis:

<i>Producer gas</i>		<i>Flue gas</i>	
CO.....	25.00%	CO ₂	12.20%
H ₂	22.00%	CO.....	0.16%
CH ₄ ..	3.60%	H ₂	0.14%
C ₂ H ₄ ..	2.80%	O ₂	7.10%
CO ₂ ..	9.20%	N ₂	80.40%
	37.40%		100.00%
	100.00%		

Calculate the weight balance of the combustion process, the heat balance of the entire unit, and the thermal efficiency on the basis of the assumptions used in Illustration 4. The heat absorbed by the kiln structure may be included with the other undetermined heat losses as a single item.

7. Limestone is burned in a continuous vertical kiln which is heated by coal burned on an external grate located beside the bottom of the kiln shaft. The limestone is charged at the top of the shaft at atmospheric temperature and gradually descends in contact with a rising stream of the flue gases from the grate. The burned lime is discharged from the bottom of the shaft at a temperature of 950° F. The flue gases, mixed with all gases and vapors evolved by the charge, leave the top of the shaft at 560° F. For each 100 lb of coal burned, 161 lb of burned lime are produced. The limestone charged has the following composition:

CaO.....	51.0%
MgO.....	2.0%
CO ₂	42.2%
Al ₂ O ₃	1.5%
SiO ₂	1.2%
H ₂ O.....	2.1%
	100.0%

The ultimate analysis of the coal is as follows:

Moisture.....	10.69%
C.....	66.62%
Net H ₂	3.18%
	1.57%
	1.91%
Corrected ash..	6.41%
Combined H ₂ O.	9.62%
	100.00%

The total heating value of the coal is 11,805 Btu per lb. The flue gases have the following composition by volume:

CO ₂	16.4%
N ₂	76.8%
O ₂	6.8%
	100.0%

The coal is burned with air at a temperature of 70° F having a percentage humidity of 80%. The barometric pressure is 29.4 in. of Hg.

The refuse from the grate contains 4.2% fixed carbon and 95.8% ash. Its sulphur content is 3.1%.

It may be assumed that in the burning process all CO_2 and water are driven from the limestone. The heat of wetting of granular limestone is negligible. It may be assumed that the sulphur burned forms SO_2 which is further oxidized and absorbed by the lime to form CaSO_4 . The mean specific heat of the burned lime is 0.21.

Calculate the complete heat and weight balances of the grate and kiln on the basis of 100 lb of coal fired.

Calculate the thermal efficiency of the process, considering the effectively utilized heat to be consumed in the decomposition of the limestone.

8. A 12-hour test was conducted on a steam generating plant with four of the boilers in operation. The data for the 12 hour test are as follows:

Proximate analysis of coal

Moisture	4.38%	Fixed carbon	48.98%
Volatile matter	29.93%	Ash (uncorrected)	16.71%
			<hr/> 100.00%

Half of the sulphur of the coal appears in the volatile matter.

Ultimate analysis of coal

Carbon	65.93%	Combined water	6.31%
Available hydrogen	3.50%	Free moisture	4.38%
Nitrogen	1.30%	Ash (corrected, sulphur free)	15.59%
Sulphur	2.99%		<hr/> 100.00%

Heating value of coal as fired (total)	11,670 Btu per lb
Weight of coal fired	119,000 lb
Temperature of coal	65° F

Proximate analysis of refuse

Moisture	4.77%	Fixed carbon	12.51%
Volatile matter	2.08%	Ash (uncorrected)	80.64%
			<hr/> 100.00%

Flue gas

CO_2	11.66%	CO	0.04%
O_2	6.52%	N_2	81.78%
			<hr/> 100.00%
Temperature			488° F

Air

Dry-bulb temperature	73° F
Wet-bulb temperature	59.4° F
Barometer	29.08 in. Hg.

Steam

Feed water	193° F
Water evaporated	1,038,400 lb
Steam pressure	137.4 lb per sq. in. gauge
Moisture in steam	1.7%

Calculate the complete weight and heat balances for this steam generating plant.

9. Calculate the complete heat balances of Illustrations 2 and 4.

CHAPTER IX

WEIGHT AND HEAT BALANCES OF CHEMICAL AND METALLURGICAL PROCESSES

The methods applied in calculating weight and heat balances are alike in principle for all industrial processes, differing only in detail. The application of these methods and principles to combustion processes has already been explained in the previous chapter. In every case the careful selection and interpretation of data require an expert knowledge of the specific industry involved. Two specific weight and heat balances will be presented in this chapter, representing the procedure applicable to chemical and metallurgical industries in general.

The illustrations selected are of considerable general educational value because they deal with complex chemical reactions whose intermediate courses are unknown. Calculations of the heat and weight balances may be carried out by the methods already described by considering only the ultimate net results produced by each complex series of reactions. For example, the heat evolved in any reaction at constant pressure and at standard temperature is equal to the difference between the sum of the heats of formation of all ultimate products and the sum of the heats of formation of all initial reactants, regardless of the intermediate course or complexity of the reactions, in accordance with the law of Hess, page 165, Chapter VI.

CHAMBER SULPHURIC ACID PLANT

The weight and heat balances of a chamber process sulphuric acid plant are selected for examination as representative of the chemical industries. Some of the operating conditions have been selected from data published by Kaltenbach.¹ In this particular problem iron pyrites is burned with air in a shelf burner. The burner gases consisting of sulphur dioxide, oxygen, and nitrogen pass through a dust chamber where suspended matter is removed, and then into the Glover tower. In the Glover tower the hot gases meet a descending stream of acids from the Gay-Lussac tower and chambers. Oxides of nitrogen lost in the system are replaced by nitric acid introduced at the top of the tower. In passing through the Glover tower the hot gases are cooled and some

¹ Chemical Age, 28, 295 (1920).

conversion of SO_2 to sulphuric acid takes place, the chamber acid is concentrated, and the oxides of nitrogen are evolved from the acids for recirculation. The mixed gases leaving the Glover tower pass into a series of large lead chambers where conversion to H_2SO_4 is completed. Finally, the oxides of nitrogen are recovered in the Gay-Lussac tower

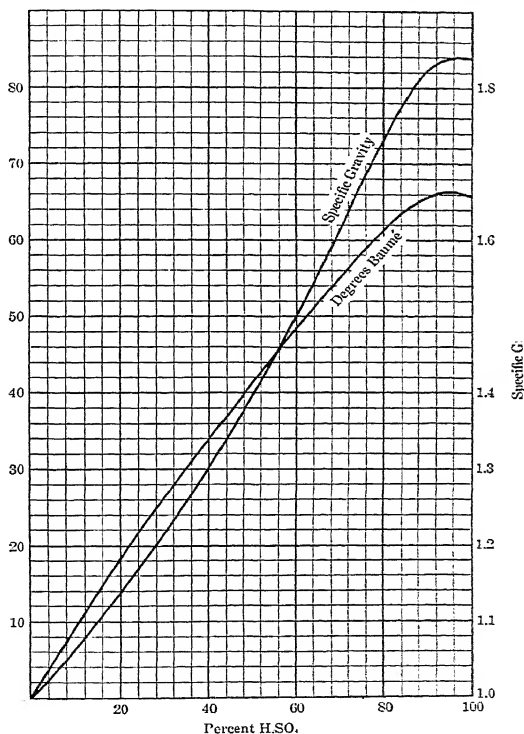


FIG. 49. Density of Aqueous Solutions of Sulphuric Acid at $15^\circ/15^\circ \text{C}$.

by passing the spent gases from the chamber countercurrent to a stream of cold sulphuric acid from the Glover tower. These different steps in the manufacture and the weight and heat balances of the burner, Glover tower, chambers and Gay-Lussac tower will each be discussed separately, the balances for each unit being based upon 100 kilograms of dry pyrites charged into the burner. The reference temperature for the

heat balances will be taken at 18°C since this corresponds to the average temperature of the air surrounding the plant during the test.

The concentration of a strong aqueous solution of sulphuric acid is usually determined by measurement of its specific gravity. Concentrations are usually expressed in terms of specific gravities or of degrees Baumé rather than in percentages. In Fig. 49 are curves relating percentages of H_2SO_4 by weight to the degrees Baumé and specific gravities, $15^{\circ}/15^{\circ}\text{C}$, of the aqueous solutions.

Illustration 1. Weight and Heat Balances of a Chamber Sulphuric Acid Plant. Pyrites, containing 85.3% FeS_2 , 2% H_2O , and 12.7% inert gangue, is burned in a shelf furnace yielding a gas containing 8.5% SO_2 , 10.0% O_2 , and 81.5% N_2 by volume. The pyrites is charged at 18°C and the air is supplied at the same temperature with a percentage humidity of 49% and at a pressure of 750 mm of Hg. The cinder leaves the burner at 400°C containing 0.42% sulphur as unburned pyrites. The pyrites burned forms Fe_2O_3 and SO_2 and the gangue passes into the cinder unchanged. The mean specific heat of the cinders is 0.18. The gases from the burner, after passing through the dust chamber, enter the Glover tower at 450°C and leave at 91°C . In the Glover tower 16% of the SO_2 in the gas is converted to H_2SO_4 . There are sprayed into the top of the Glover tower, per 100 kg of moisture-free pyrites charged:

- 182 kg of aqueous sulphuric acid at 25°C from the chambers, containing 64.0% H_2SO_4 and 36% H_2O .
- 580 kg of mixed acid at 25°C from the Gay-Lussac tower, containing 77% H_2SO_4 , 22.1% H_2O , and 0.885% N_2O_5 .
- 1.31 kg of aqueous nitric acid at 25°C , containing 36% HNO_3 and 64% H_2O .

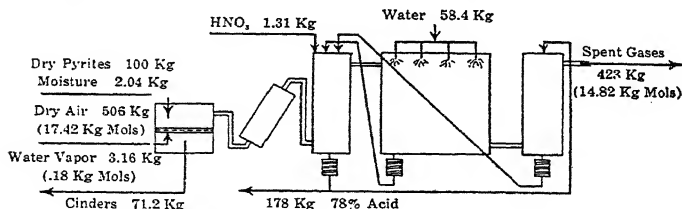


Fig. 50. Weight Balance of an Entire Sulphuric Acid Plant.

Acid leaves the bottom of the Glover tower, free from oxides of nitrogen, at a temperature of 125°C , and containing 78.0% H_2SO_4 and 22% H_2O . This acid is cooled to 25°C , part of it is returned to the top of the Gay-Lussac tower, and the remainder is withdrawn as the final product of the plant. The gases leaving the Glover tower are passed through a series of four chambers and finally enter the Gay-Lussac tower, at 40°C . Spray water is introduced in at the tops of the various chambers at 18°C . The acid formed in the chambers is withdrawn from the first chamber at 68°C , containing 64.0% H_2SO_4 . This acid is cooled to 25°C and all fed into the top of the Glover tower. Part of the Glover acid after cooling to 25°C is returned to the top of the Gay-Lussac tower. The Gay-Lussac acid leaves the bottom of the tower at 27°C and is all fed to the top of the Glover tower at 25°C . The spent gases leave

the top of the Gay-Lussac tower at 30° C. The flow-chart of the entire process is shown diagrammatically in Fig. 50, page 288.

Calculate weight and heat balances of the entire plant and of each of the following units, all based on 100 kg of moisture-free pyrites charged:

- The burner.
- The Glover tower.
- The four chambers as a single unit.
- The Gay-Lussac tower.

WEIGHT BALANCE OF ENTIRE PLANT

Before discussing the weight and heat balances of the individual units in the sulphuric acid plant it is desirable to calculate the weight balance of the entire plant in order to have in mind a perspective of the entire process. This balance is represented by the following entries:

<i>Input</i>		<i>Output</i>
Dry ore	Moisture in air	Acid produced
Moisture in ore	Nitric acid	Dry spent gases
Dry air	Spray water	Cinder

1. Weight of cinder formed.

Basis: 100 kg of moisture-free pyrites charged.

Weight of pyrites as charged = $\frac{100}{0.98} = \dots\dots\dots$	102 kg
Weight of FeS_2 charged = $102 \times 0.853 = \dots\dots\dots$	87 kg
or $87/120 = \dots\dots\dots$	0.726 kg-mol
Weight of gangue charged = $102 \times 0.127 = \dots\dots\dots$	13 kg
Percentage S in cinders = $\dots\dots\dots$	0.42%
Percentage FeS_2 in cinders = $\dots\dots\dots$	
$\frac{0.42}{32} \times \frac{1}{2} \times 120 = \dots\dots\dots$	0.78%

Let x = kilograms of FeS_2 in cinders.

Weight of FeS_2 oxidized = $(87 - x)$ kg or $(87 - x)/120$ kg-mols

Fe_2O_3 formed = $\frac{87 - x}{120} \times \frac{1}{2} \times 159.7 = (58 - 0.667x)$ kg

Weight of cinder = $13.0 + x + (58 - 0.667x) = (71 + 0.333x)$ kg

Weight of FeS_2 in cinder =

$x = 0.0078(71 + 0.333x)$ or, $x = \dots\dots\dots$ 0.56 kg

or = $0.56/120 = 0.0048$ kg-mol

Fe_2O_3 in cinder = $58 - (0.667 \times 0.56) = \dots\dots\dots$ 57.63 kg

or = $57.63/159.7 = 0.361$ kg-mol

Total weight of cinder = $\dots\dots\dots$ 71.2 kg

2. Weight of dry burner gases.

Sulphur Balance. *Basis:* 100 kg of dry pyrites charged.

FeS_2 burned = $0.726 - 0.005 = \dots\dots\dots$ 0.721 kg-mol

S burned = $0.721 \times 2 = \dots\dots\dots$ 1.442 kg-mols

S per kg-mol of burner gas = $\dots\dots\dots$ 0.085 kg-mol

Dry burner gas = $\frac{1.442}{0.085} = \dots\dots\dots$ 16.95 kg-mols

$\text{SO}_2 = 16.95 \times 0.085 =$	$1.441 \text{ kg-mols or } \times 64 =$	92.2 kg
$\text{O}_2 = 16.95 \times 0.100 =$	$1.70 \text{ kg-mols or } \times 32 =$	54.4 kg
$\text{N}_2 = 16.95 \times 0.815 =$	$13.81 \text{ kg-mols or } \times 28.2 =$	389.8 kg
Total dry gases =	16.95 kg-mols or	536.4 kg

3. Weight of dry air used.

Nitrogen Balance:

Nitrogen in burner gas =	13.81 kg-mols
Air introduced = $\frac{13.81}{0.79} =$	17.5 kg-mols
or $17.42 \times 29 =$	506 kg

4. Weight of water vapor in dry air. The air supply enters at 18°C , 49% percent-age humidity, and 750 mm pressure. From Fig. 10 the molal humidity is 0.0101.

Water vapor in air = $0.0101 \times 17.5 =$	0.176 kg-mol
or $0.176 \times 18 =$	3.16 kg

5. H_2SO_4 produced in system. Sulphuric acid is formed only in the Glover tower and in the chambers.

SO_2 entering Glover tower =	1.44 kg-mols
SO_2 converted to acid in Glover tower = $1.44 \times 0.16 =$	0.230 kg-mol
H_2SO_4 formed in Glover tower = $0.230 \times 98.1 =$	22.6 kg
H_2SO_4 in acid from chambers = $182 \times 0.64 =$	116.5 kg
Total H_2SO_4 formed =	139.1 kg
or = $139.1/98 =$	1.42 kg-mols
Total product of aqueous acid, 78% $\text{H}_2\text{SO}_4 =$	
$139.1/0.78 =$	178 kg

6. Weight of spray water in chambers.

Water Balance:

Output

The small amount of water vapor in the gases from the Gay-Lussac tower may be neglected. On this basis all water leaves the process in the 78% acid product.

H_2O used in forming $\text{H}_2\text{SO}_4 = 1.42 \text{ kg-mols}$	
or $1.42 \times 18 =$	25.5 kg
H_2O in aqueous acid = $178 \times 0.22 =$	39.0 kg
Total H_2O output =	64.5 kg

Input

H_2O in ore = $102 \times 0.02 =$	2.04 kg
H_2O in air =	3.16 kg
H_2O from aqueous nitric acid = $1.31 \times 0.64 =$	0.84 kg

It is assumed that the HNO_3 introduced is completely decomposed into H_2O , NO , and O_2 .

$$\begin{aligned}\text{HNO}_3 \text{ introduced} &= 1.31 \times 0.36 = 0.47 \text{ kg or} \\ &0.47/63 = 0.0075 \text{ kg-mol}\end{aligned}$$

$$\text{H}_2\text{O formed from HNO}_3 = 0.0075/2 = 0.0037 \text{ kg-mol or} = \dots\dots\dots$$

$$0.067 \text{ kg}$$

$$\text{Total H}_2\text{O input accounted for} = \dots\dots\dots 6.11 \text{ kg}$$

$$\text{Water supplied by sprays} = 64.5 - 6.1 = \dots\dots\dots 58.4 \text{ kg}$$

7. Gases leaving Gay-Lussac tower. The gases leaving the acid plant consist of SO_2 , O_2 , and N_2 from the burner and the oxides of nitrogen which are supplied by the nitric acid and lost from the system. Most of the SO_2 and a corresponding amount of oxygen are removed from the burner gases to form H_2SO_4 . It is assumed that no water vapor leaves the Gay-Lussac tower because of the great affinity of strong, cold sulphuric acid for water.

$$\text{SO}_2 \text{ from burner} = \dots\dots\dots 1.441 \text{ kg-mols}$$

$$\text{SO}_2 \text{ forming H}_2\text{SO}_4 = \dots\dots\dots 1.42 \text{ kg-mols}$$

$$\text{SO}_2 \text{ in gases leaving} = \dots\dots\dots 0.021 \text{ kg-mol} = 1.34 \text{ kg}$$

$$\text{O}_2 \text{ in burner gases} = \dots\dots\dots 1.70 \text{ kg-mols}$$

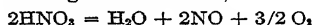
$$\text{O}_2 \text{ used in oxidizing SO}_2 = 1.42/2 = \dots\dots\dots 0.71 \text{ kg-mol}$$

$$\text{O}_2 \text{ from burner in gases leaving} = \dots\dots\dots 0.99 \text{ kg-mol} = 31.9 \text{ kg}$$

$$\text{N}_2 \text{ in gases from burner} = \dots\dots\dots 13.81 \text{ kg-mols} = 389.8 \text{ kg}$$

$$\text{HNO}_3 \text{ decomposed} = \dots\dots\dots 0.0075 \text{ kg-mol}$$

According to the reaction,



$$\text{O}_2 \text{ from HNO}_3 = 0.0075(3/4) = \dots\dots\dots 0.0056 \text{ kg-mol} = 0.18 \text{ kg}$$

$$\text{NO from HNO}_3 = \dots\dots\dots 0.0075 \text{ kg-mol} = 0.22 \text{ kg}$$

Total gases leaving:

$$\text{SO}_2 \dots\dots\dots 0.0021 \text{ kg-mol} \quad 1.3 \text{ kg}$$

$$\text{O}_2 \dots\dots\dots 0.995 \text{ kg-mol} \quad 31.9 \text{ kg}$$

$$\text{NO} \dots\dots\dots 0.0075 \text{ kg-mol} \quad 0.22 \text{ kg}$$

$$\text{N}_2 \dots\dots\dots 13.81 \text{ kg-mols} \quad 389.8 \text{ kg}$$

$$\text{Total} \dots\dots\dots 14.82 \text{ kg-mols} \quad 423.2 \text{ kg}$$

Weight Balance of Entire Plant.

<i>Input</i>		<i>Output</i>	
Dry pyrites	100.0 kg	Cinder	71.2 kg
H ₂ O in pyrites	2.04 kg	Spent gases (14.82 kg-mols)	423.2 kg
Dry air (17.42 kg-mols)	506. kg	Acid (78% H ₂ SO ₄)	178.0 kg
H ₂ O in air (0.176 kg-mol)	3.16 kg		
Nitric acid	1.31 kg	Total	672.4 kg
Spray water	58.4 kg		
Total	670.9 kg		

This weight balance is summarized in Fig. 50

WEIGHT BALANCE OF BURNER

Input		Output	
Dry ore.....	100 kg	Cinder.....	71.2 kg
Moisture in ore.....	2.04 kg	Dry gases.....	536.4 kg
Dry air (17.42 kg-mols) ..	506. kg	Water vapor (3.16 +	
Moisture in air.....	3.16 kg	2.04) =	5.2 kg
Total.....	611.2 kg	Total.....	612.8 kg

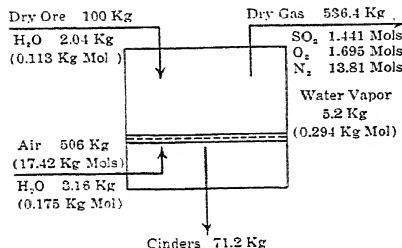


FIG. 51. Weight Balance of Pyrites Burner.

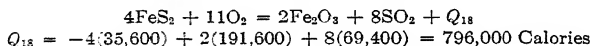
This weight balance is summarized in Fig. 51.

HEAT BALANCE OF BURNER

The heat balance of the burner includes the heat of combustion of FeS₂ to Fe₂O₃ and SO₂ and the heat content of the water vapor in the air as the only important sources of heat. The heat output is distributed as sensible heat of the outgoing cinders and dry gases and as total heat content of outgoing water vapor. The heat losses include radiation from the

dust chamber and flues up to the entrance of the Glover tower where the temperature of the burner gases, 450° C, was measured.

1. Heat of combustion of pyrites. The reaction involved in the combustion of pyrites and the corresponding standard heat of reaction are as follows:



The heat of combustion per mol of FeS₂ is then 199,000 Calories.

FeS₂ actually burned = 0.721 kg-mol.

Standard heat of combustion of FeS₂ burned =

$$0.721 \times 199,000 = \dots\dots\dots 143,400 \text{ Calories}$$

2. Heat content of water vapor in air. From Fig. 10, dew-point = 7° C.

Heat of vaporization at 7° C = 10,630 Calories per kg-mol.

Total heat content =

$$0.176[10,630 - 18(18 - 7) + 8.4(18 - 7)] = \dots\dots\dots 1,850 \text{ Calories}$$

3. Heat content of cinders = 71.2 × 0.18(450 - 18) = 5,540 Calories

4. Heat content of dry burner gas.

Mean heat capacity between 18° C and 450° C:

(From Fig. 12, page 116).

$$\text{SO}_2 = 1.44 \times 10.1 = \dots\dots\dots 14.6 \text{ Calories per } ^\circ\text{C}$$

$$\text{O}_2 \text{ and N}_2 = 15.51 \times 7.1 = \dots\dots\dots 110.2 \text{ Calories per } ^\circ\text{C}$$

$$\text{Total} = \dots\dots\dots 124.8 \text{ Calories per } ^\circ\text{C}$$

$$\text{Heat content} = 124.8(450 - 18) = \dots\dots\dots$$

$$54,000 \text{ Calories}$$

5. Heat content of water vapor in burner gases.

Water vapor present = $5.2/18 = 0.29$ kg-mol.

Molal humidity = $0.29/16.95 = 0.017$.

From Fig. 10, dew-point = 15°C .

Heat of vaporization at $15^{\circ}\text{C} = 10,720$ Calories per kg-mol.

Mean molal heat capacity of water vapor (15°C – 450°C) = 8.6 Calories per $^{\circ}\text{C}$

Heat content = $0.29 [10,720 - 18(18 - 15) + 8.6(450 - 15)] = 4170$ Calories

Summary Heat Balance of Burner.

Input

1. Heat of combustion of pyrites =	143,400 Calories	98.7%
2. Heat content of water vapor in air =	1,850 Calories	1.3%
Total input =	145,250 Calories	100.0%

Output

1. Heat content of cinders =	5,540 Calories	3.8%
2. Heat content of dry burner gas =	54,000 Calories	37.1%
3. Heat content of water vapor in gases =	4,170 Calories	2.9%
4. Heat loss (by difference) =	81,540 Calories	56.2%
Total output =	145,250 Calories	100.0%

This heat balance is summarized in Fig. 52.

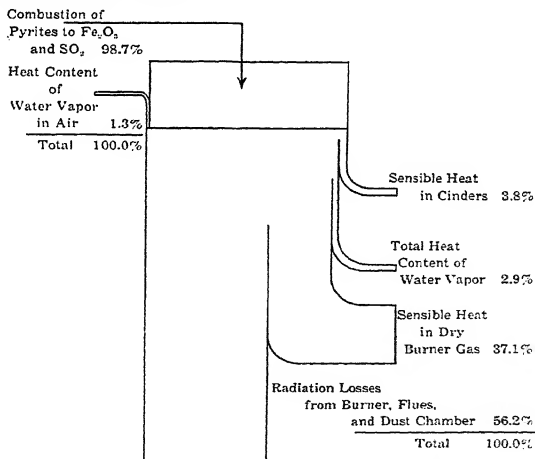


FIG. 52. Heat Balance of Pyrites Burner.

WEIGHT BALANCE OF GLOVER TOWER

The useful functions of the Glover tower are as follows:

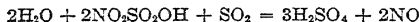
1. Cooling of burner gases before being blown into the chambers.
2. Conversion of about 16% of SO_2 in burner gas to H_2SO_4 .

3. Mixing of Gay-Lussac and chamber acids and nitric acid.
4. Evolution of oxides of nitrogen from Gay-Lussac acid.
5. Concentration of chamber acid.

At the top of the tower, mixing of the Gay-Lussac and chamber acids takes place with the release of the oxides of nitrogen from the Gay-Lussac acid when this acid is heated and diluted. Nitric acid is also added to make up for losses of the oxides of nitrogen through leakage in the system and incomplete absorption in the Gay-Lussac tower. The oxides of nitrogen are present as a mixture of NO and NO₂, but since the equilibrium mixture gradually changes owing to variation in temperature and in oxygen content it is customary to assume that the oxides of nitrogen leave the Glover tower as NO. The released oxides of nitrogen react in the vapor state with SO₂, oxygen and water vapor, forming liquid nitrosyl-sulphuric acid



Because of the high concentration of SO₂ in the Glover tower, the decomposition of this nitrosyl-sulphuric acid is complete, forming sulphuric acid according to the equation



The second reaction proceeds much more rapidly than the first in mols per unit volume of space, chiefly because it is a reaction which proceeds in the liquid phase. The high concentration in the liquid state permits a more rapid rate of reaction, other conditions being the same. The final concentration of the Glover acid takes place at the hottest zone near the bottom of the tower and the acid finally leaves as 78% H₂SO₄.

The input of the weight balance includes the gases from the burner, the chamber acid, the make-up nitric acid introduced, and the Gay-Lussac acid. The output includes the Glover acid and the gases leaving to enter the chambers.

Input to Glover Tower

Basis: 100 kg of moisture-free pyrites charged.

1. Dry burner gases = 16.95 kg-mols =	536.4 kg
2. Water vapor in burner gases = 0.29 kg-mol =	5.2 kg
3. Chamber acid (64% H ₂ SO ₄ ; 36% H ₂ O) =	182 kg
4. Nitric acid (36% HNO ₃) =	1.31 kg
5. Gay-Lussac acid (77% H ₂ SO ₄ ; 22.1% H ₂ O; and 0.885% N ₂ O ₅) =	580 kg
Total input =	1304.9 kg

Output

1. Weight of Glover acid. The H₂SO₄ leaving the Glover tower in 78% acid includes that from the chamber and Gay-Lussac acids and that formed by conversion of SO₂ to H₂SO₄ in the tower already calculated to be 0.230 kg-mol.

H ₂ SO ₄ from chambers = 182 × 0.64 =	116.4 kg
H ₂ SO ₄ from Gay-Lussac acid = 580 × 0.77 =	446 kg
H ₂ SO ₄ formed in tower = 0.230 × 98 =	22.6 kg
Total H ₂ SO ₄	585.0 kg

Weight of 78% acid leaving Glover tower = $\frac{585}{0.78}$ = 750 kg

2. **Weight of dry gases leaving the Glover tower.** The weight and composition of the dry burner gases in passing through the Glover tower is changed owing to the disappearance of some SO_2 and the corresponding amount of oxygen in the formation of SO_3 and to the evolution of NO and O_2 due to the decomposition of nitric acid and the release of the oxides of nitrogen from the Gay-Lussac acid.

Dry burner gases entering tower:

$\text{SO}_2 =$	1.44 kg-mols
$\text{O}_2 =$	1.70 kg-mols
$\text{N}_2 =$	13.81 kg-mols
Total =	16.95 kg-mols

SO_2 converted to H_2SO_4 in tower =	0.230 kg-mol
SO_2 leaving tower = $1.44 - 0.230 =$	1.21 kg-mols
O_2 used in forming $\text{SO}_3 = 0.230/2 =$	0.115 kg-mol
O_2 remaining from burner gases = $1.70 - 0.115 =$	1.58 kg-mols

Nitric acid decomposed =

$1.31 \times 0.36 = 0.472$ kg or	0.0075 kg-mol
$2\text{HNO}_3 = \text{H}_2\text{O} + 2\text{NO} + \frac{1}{2}\text{O}_2$	
O_2 from $\text{HNO}_3 = 0.0075 \times \frac{1}{2} =$	0.0038 kg-mol
NO from $\text{HNO}_3 =$	0.0075 kg-mol
H_2O from $\text{HNO}_3 = 0.0075/2 =$	0.0038 kg-mol

N_2O_3 from Gay-Lussac acid =

$580 \times 0.00885 = 5.13$ kg or	0.0675 kg-mol
$\text{N}_2\text{O}_3 = 2\text{NO} + \frac{1}{2}\text{O}_2$	
O_2 from $\text{N}_2\text{O}_3 = 0.0675/2 =$	0.0338 kg-mol
NO from $\text{N}_2\text{O}_3 =$	0.1350 kg-mol
Total O_2 leaving = $1.58 + 0.0038 + 0.0338 =$	1.62 kg-mols
Total NO leaving = $0.0075 + 0.1350 =$	0.143 kg-mol

Total dry gases leaving

$\text{SO}_2 = 1.21$ kg-mols or $\times 64 =$	77.5 kg
$\text{O}_2 = 1.62$ kg-mols or $\times 32 =$	51.8 kg
$\text{NO} = 0.143$ kg-mol or $\times 30 =$	4.29 kg
$\text{N}_2 = 13.81$ kg-mols or $\times 28.2 =$	389.8 kg
Total 16.78 kg-mols or	523.6 kg

Total weight of dry gases leaving Glover tower = 523.6 kg

3. **Water vapor in the gases leaving the Glover tower.** The weight of water vapor in the gases leaving the Glover tower is calculated on the basis of a water balance. Water enters as vapor in the gases, as water in the Gay-Lussac and chamber acids and associated with the nitric acid as HNO_3 and as water. The 0.230 kg-mol of H_2SO_4 formed in the tower requires 0.230 kg-mol of H_2O or 4.15 kg. The 78% acid leaving requires $(750)(0.22) = 165$ kg water.

The 1.31 kg of 36% nitric acid charged yields upon dehydration and decomposition $.84 + 0.07 = 0.91$ kg H_2O .

Water Balance:

<i>Input</i>	
In gas (0.289 kg-mol) =	5.2 kg
In chamber acid (182) (0.36) =	65.5 kg
In Gay-Lussac acid $580 \times 0.221 =$.	129.0 kg
From nitric acid =	0.9 kg
Total.	200.6 kg

Output

In 78% acid	165.0 kg
In formation of H_2SO_4	4.1 kg
In water vapor (by difference)	31.5 kg
Total.	200.6 kg

Total water vapor in gases leaving 31.5 kg
 or $31.5/18 =$ 1.75 kg-mols

Molal humidity of gases leaving = $\frac{1.75}{16.78} = 0.103$

Dew-point of gases leaving (From Fig. 9) = 113° F or 45° C

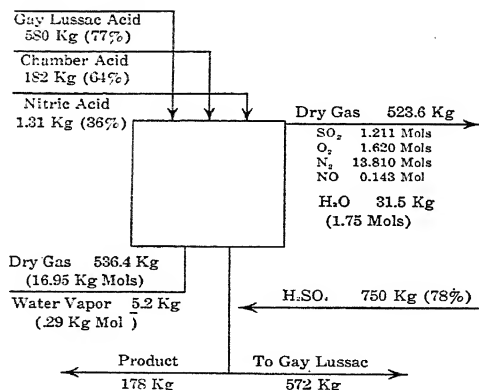


FIG. 53. Weight Balance of Glover Tower.

Summary Weight Balance of Glover Tower.

<i>Input</i>	
Dry gases (16.95 kg-mols) =	536.4 kg
Water vapor (0.29 kg-mol) =	5.2 kg
Chamber acid (64% H_2SO_4) =	182.0 kg
Nitric acid (36% HNO_3) =	1.31 kg
Gay-Lussac acid =	580.0 kg
Total =	1304.9 kg

Output

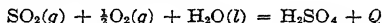
Dry gases =	523.6 kg
Water vapor =	31.5 kg
Glover acid (78% H_2SO_4) =	750.0 kg
Total =	1305.1 kg

This weight balance is summarized in Fig. 53.

HEAT BALANCE OF GLOVER TOWER

In addition to the heat contents of all materials entering and leaving, the credit side of the heat balance of the Glover tower includes heat evolved in the formation of H_2SO_4 within the tower. This acid goes into solution but at the same time some water leaves the solution, the net effect being one of concentration and hence requiring the input of heat. In addition, heat is required to remove the oxides of nitrogen from solution and to decompose them into NO and O_2 . It will be assumed that all oxides of nitrogen, both from the Gay-Lussac and the make-up nitric acids, are decomposed and leave the Glover tower as NO.

1. Heat evolved in formation of H_2SO_4 . Sulphuric acid is formed from SO_2 gas, liquid H_2O , and oxygen. Actually the conversion takes place in two steps with intermediate formation of nitrosyl-sulphuric acid. However, the net effect is the same as though the reaction proceeded as follows:



$$Q = -69,400 + 0 - 68,310 + 189,750 = +52,040 \text{ Calories (kg-mols)}$$

$$\text{Heat of formation of } \text{H}_2\text{SO}_4 = 0.230 \times 52,040 = \dots\dots\dots 11,950 \text{ Calories}$$

2. Heat absorbed in concentrating acid. The sulphuric acid formed in the tower is diluted by the acid already present to form 78% acid leaving. The chamber acid entering at 64% is concentrated to 78%. The Gay-Lussac acid yields aqueous sulphuric acid containing 77/0.991 or 77.7% H_2SO_4 . This is concentrated to 78% acid. The net result of these changes is a concentrating effect.

The net heat effect of the concentration changes in the Glover tower may be calculated from integral heat of solution data by the method discussed on page 180. The heat evolved is the difference between the total heat evolved in forming each of the entering acid solutions from H_2SO_4 and H_2O and that evolved in forming the solution leaving from H_2SO_4 and H_2O . These thermal effects may be calculated from the integral heat of solution data plotted in Fig. 54, page 298. This curve was plotted from data of the International Critical Tables, Vol. V.

Molal integral heats of solution of H_2SO_4 :

Concentration 64% H_2SO_4 =	11,800 Calories per kg-mol
Concentration 77.7% H_2SO_4 =	8,700 Calories per kg-mol
Concentration 78% H_2SO_4 =	8,600 Calories per kg-mol

Total heat of solution of chamber acid =

$$\frac{182 \times 0.64}{98} \times 11,800 = \dots\dots\dots 14,000 \text{ Calories}$$

Total heat of solution of Gay-Lussac acid =

$$\frac{580 \times 0.77}{98} \times 8,700 = \dots\dots\dots 39,700 \text{ Calories}$$

Total heat of solution of entering acids =

$$53,700 \text{ Calories}$$

Total heat of solution of Glover acid leaving =

$$\frac{750 \times 0.78}{95} \times 8600 = 51,300 \text{ Calories}$$

Heat evolved in concentration of acid =

$$51,300 - 53,700 = \dots\dots\dots -2400 \text{ Calories}$$

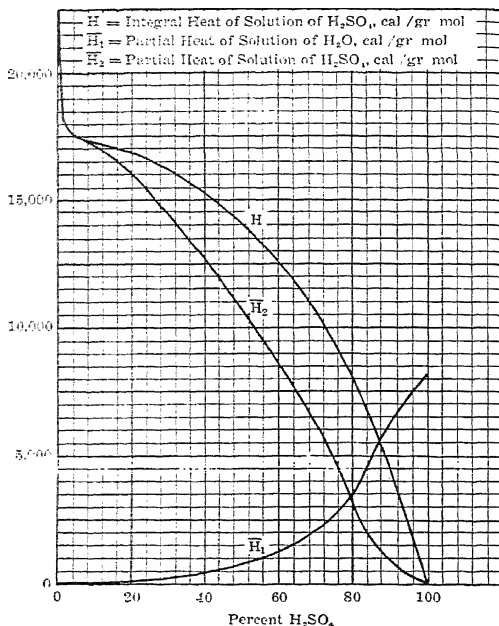


FIG. 54. Partial and Integral Heats of Solution of Aqueous Solutions of Sulphuric Acid at 20° C.

The net heat consumed in release and decomposition is 2400 calories, which should be placed on the output side of the heat balance. The large amount of heat required for the concentration of chamber acid is offset by the heat evolved when the H_2SO_4 formed in the tower is dissolved.

3. Heat absorbed in release and decomposition of N_2O_3 from Gay-Lussac acid. The oxides of nitrogen enter the Glover tower as recovered nitrosyl-sulphuric acid from the Gay-Lussac tower and as make-up nitric acid. The Gay-Lussac acid may be considered to consist of 0.0677 kg-mol of N_2O_3 dissolved in 129 kg (7.15 kg-mols) of water. This concentration corresponds to 106 mols of water per mol N_2O_3 . The thermal effects in the evolution of the N_2O_3 from solution and its decomposition may be calculated from the following thermochemical data:

<i>Formula</i>	<i>State</i>	<i>Heat of Formation Calories per kg-mol</i>	<i>Mols of Water</i>	<i>Solution, Calories</i>
NO	<i>g</i>	-21,600		
N ₂ O ₃	<i>g</i>	-21,400	100	+28,900
NO ₂	<i>g</i>	-7,420		
N ₂ O ₄	<i>g</i>	-1,860		
N ₂ O ₅	<i>g</i>	+1,200		
HNO ₃	<i>l</i>	+42,450	6.22	7,000

Heat absorbed in evolution of N₂O₃ from solution in the Gay-Lussac acid =
 $0.0677 \times 28,900 = 1960$ Calories

This entry is not exact since it has been assumed that the heat of solution of N₂O₃ is the same in 77.7% H₂SO₄ acid as it is in water, which is a poor approximation.

The N₂O₃ is assumed to break down entirely to NO and O₂; this is also an approximation. However, in view of the relatively small heat effects involved these approximations seem justified.



$$\text{Q} = -(-21,400) + 2(-21,600) = -21,800 \text{ Calories (kg-mols)}$$

Heat absorbed in decomposition of N₂O₃ = $0.0677 \times 21,800$
 = 1480 Calories

Total heat absorbed in release and decomposition of N₂O₃ = 3440 Calories

4. Heat absorbed in decomposition of nitric acid. The nitric acid consists of 0.0075 kg-mol HNO₃ dissolved in 0.0466 kg-mol water, corresponding to 6.22 mols water per mol of HNO₃. The acid may be considered to be separated into its liquid components, HNO₃ and water, and then decomposed according to the following reaction:



$$\text{Q} = -42,450 + 34,155 + (-21,600) = -29,895 \text{ Calories (kg-mols)}$$

Heat absorbed in separating HNO₃ from H₂O = $0.0075 \times 7000 = \dots\dots\dots$ 52 Calories

Heat absorbed in decomposition of HNO₃ = $0.0075 \times 29,895 = \dots\dots\dots$ 224 Calories

Total heat absorbed = $\dots\dots\dots$ 276 Calories

The decomposition of the oxides of nitrogen is of particular interest because of their endothermic heats of formation.

5. Heat input in burner gases. This has already been calculated as the heat output of the burner, page 293, = $\dots\dots\dots$ 58,170 Calories

6. Heat content of chamber acid.

Total heat capacity (from Fig. 55) = $\dots\dots\dots$ 0.50 Calories per kg per °C

Heat content = $182 \times 0.50 \times (25 - 18) = \dots\dots\dots$ 640 Calories

7. Heat content of Gay-Lussac acid.

Total heat capacity (Fig. 55) = $\dots\dots\dots$ 0.45 Calories per kg per °C

Heat content = $580 \times 0.45(25 - 18) = \dots\dots\dots$ 1830 Calories

This calculation neglects the effect of the oxides of nitrogen on the heat capacity of the Gay-Lussac acid.

8. Heat content of nitric acid. From Fig. 15, page 121, the specific heat of 36% nitric acid is 0.70.

$$\text{Heat content} = 1.31 \times 0.70(25 - 18) = \dots$$

7 Calories

9. Heat content of dry gases leaving.

Mean heat capacity between 18° C and 91° C.

(From Fig. 12, page 116).

$$\text{SO}_2 \quad 1.21 \times 9.3 = \dots\dots\dots 11.3$$

$$\text{N}_2, \text{NO}, \text{O}_2 \quad 15.57 \times 6.95 = \dots\dots 108.2$$

$$\text{Total heat capacity} = \dots\dots\dots 119.5$$

$$\text{Heat content} = 119.5(91 - 18) = \dots\dots\dots 8720 \text{ Calories}$$

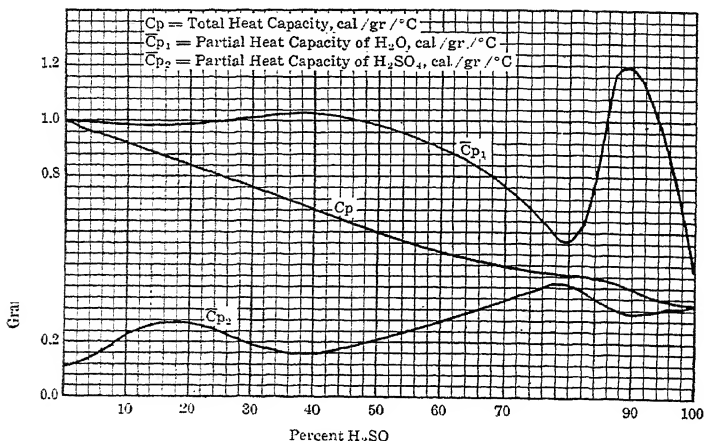


FIG. 55. Partial and Total Heat Capacities of Aqueous Solutions of Sulphuric Acid at 20° C.

10. Total heat content of water vapor leaving Glover tower.

The water vapor leaves at 91° C having a dew-point of 45° C.

Heat of vaporization at 45° C (Fig. 9) = 10,290 Calories per kg.

Mean molal heat capacity of vapor between 45° C and 91° C = 8.4.

Heat content =

$$1.75[10,290 + 18(45-18) + 8.4(91-45)] = \dots\dots\dots$$

20,400 Calories

11. Heat absorbed in cooling outgoing acid.

Heat capacity (Fig. 55) = 0.44 Calories per kg per °C, neglecting the temperature coefficient of the heat capacity.

$$\text{Heat absorbed} = 750 \times 0.44(125-25) = \dots\dots\dots$$

33,000 Calories

12. Heat content of outgoing acid = $750 \times 0.44(25-18) =$.

2300 Calories

Summary Heat Balance of Glover Tower.

<i>Input</i>		
Heat content of dry burner gases	54,000 Calories	74.4%
Heat content of water vapor from burner . . .	4,170 Calories	5.7%
Heat content of chamber acid	640 Calories	0.9%
Heat content of Gay-Lussac acid	1,830 Calories	2.5%
Heat content of nitric acid	7 Calories	0.0%
Heat evolved in formation of H_2SO_4	11,950 Calories	16.5%
Total	72,597 Calories	100.0%

<i>Output</i>		
Heat content of dry gases	8,720 Calories	12.0%
Heat content of water vapor in gases	20,400 Calories	28.1%
Heat content of acid leaving cooler	2,300 Calories	3.2%
Heat absorbed in concentration of acid	2,400 Calories	3.3%
Heat absorbed in decomposition of nitric acid .	276 Calories	0.4%
Heat absorbed in release and decomposition of N_2O_5 from Gay-Lussac acid	3,440 Calories	4.7%
Heat absorbed by outgoing acid cooler	33,000 Calories	45.5%
Heat losses (by difference)	2,061 Calories	2.8%
Total	72,597 Calories	100.0%

This heat balance is summarized in Fig. 56.

It will be seen that over one-half of the available heat energy in the Glover tower is absorbed by the concentrated acid. This acid must be cooled before it can be used for absorption of gases in the Gay-Lussac tower and before storage. The cooling of this acid represents one of the difficult problems in acid manufacture, in the development of a heat interchanger which will withstand hot concentrated sulphuric acid and at the same time permit a rapid transfer of heat.

WEIGHT BALANCE OF CHAMBERS

It would be proper to consider the weight and heat balances of each chamber separately, but to avoid needless repetition all four chambers will be considered as a unit. In the chambers, H_2O , SO_2 , and O_2 are removed from the gases to form

Basis: 100 kg of dry pyrites charged.

 H_2SO_4 formed in chambers = 116.5 kg or 1.19 kg-mols.

<i>Gas Entering</i>	<i>Gas Removed</i>	<i>Dry Gas Leaving</i>
SO_2 1.21 kg-mols	1.19 kg-mols	0.021 kg-mol
O_2 1.62 kg-mols	0.595 kg-mol	1.025 kg-mols
NO 0.143 kg-mol		0.143 kg-mol
N_2 13.81 kg-mols		13.81 kg-mols
H_2O 1.75 kg-mols	1.19 kg-mols	
Total =		15.00 kg-mols

Water vapor leaving. The water entering with the gases and from the sprays is used in the formation of H_2SO_4 and dilution of the H_2SO_4 to form the chamber acid.

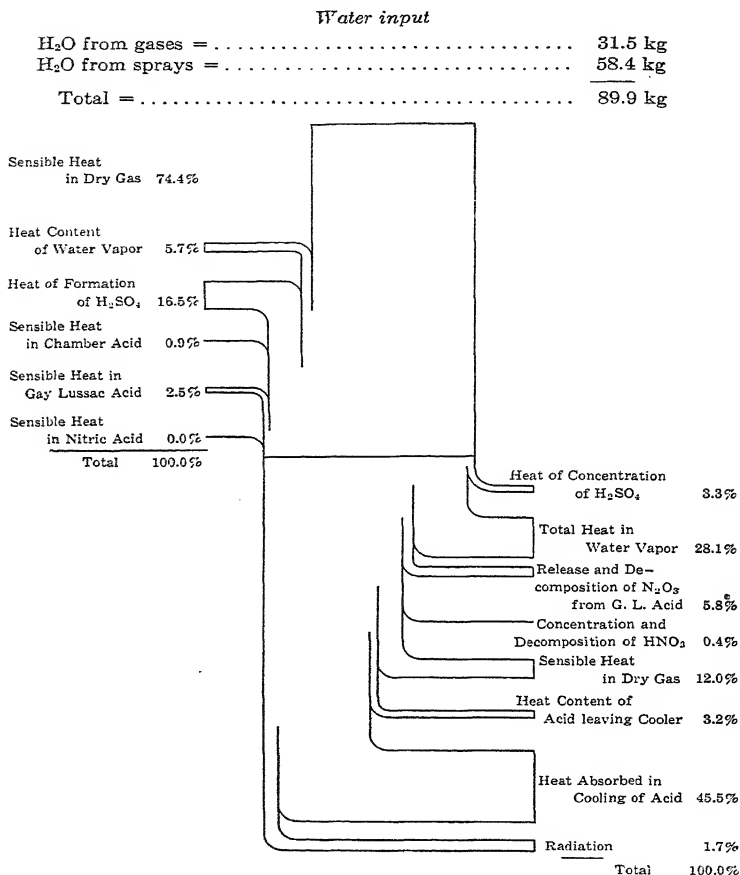


FIG. 56. Heat Balance of Glover Tower.

<i>Water output</i>	
H ₂ O to form H ₂ SO ₄ = 1.19×18 =	21.4 kg
H ₂ O in chamber acid = 182×0.36 =	65.5 kg
Output accounted for =	86.9 kg
H ₂ O in gases leaving = $89.9 - 86.9$ =	3.0 kg
or $3.0/18$ =	0.167 kg-mol

Mols of dry gases leaving =	15.0 kg-mols
Molal humidity = $0.167/15.0 =$	0.011
Dew-point (Fig. 10) =	46° F or 8° C

Summary of Weight Balance of Chambers.

<i>Entering</i>		<i>Leaving</i>	
SO ₂ (1.21 kg-mols)	77.5 kg	SO ₂ (0.021 kg-mol)	1.3 kg
O ₂ (1.62 kg-mols)	51.8 kg	O ₂ (1.025 kg-mols)	32.8 kg
N ₂ (13.81 kg-mols)	390.0 kg	N ₂ (13.81 kg-mols)	390.0 kg
H ₂ O (1.75 kg-mols)	31.5 kg	H ₂ O (0.168 kg-mol)	3.0 kg
NO (0.143 kg-mol)	4.3 kg	NO (0.143 kg-mol)	4.3 kg
Spray water	58.4 kg	Acid	182.0 kg
Total	613.5 kg	Total	613.4 kg

This weight balance is summarized in Fig. 57.

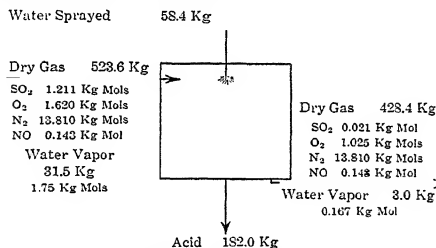
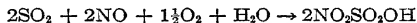


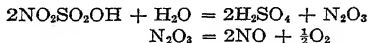
Fig. 57. Weight Balance of Chambers.

HEAT BALANCE OF CHAMBERS

The first reaction proceeding in the chambers is a gaseous reaction between the SO₂, H₂O, O, and NO gases in contact with the water spray forming nitrosyl-sulphuric acid.



This reaction is favored by high concentrations of SO₂ and NO. The acid spray is swept against the side walls of the chamber where the spray is condensed owing to cooling, and by dilution with water, H₂SO₄ is formed with the release of the oxides of nitrogen.



The first of these reactions proceeds in the liquid phase and is favored by a high concentration of water brought in by the spray and condensed upon the side walls.

In calculating the heat evolved in the chamber reactions only the final, net effects need be considered. It will be assumed that the oxides of nitrogen ultimately leave the chambers in the same form in which they entered, NO. This assumption is not exact because some oxidation of NO to N₂O₃ probably takes place at the relatively low temperatures of the last chamber. The ultimate effects of the reactions in the chambers are then the production of H₂SO₄ from SO₂, O₂, and H₂O and the dissolution of this acid to form an aqueous solution containing 64% H₂SO₄.

Reference temperature: 18° C.

Basis: 100 kg of dry pyrites charged.

1. Heat evolved in formation of H_2SO_4 . From item 1 of the heat balance of the Glover tower, the heat evolved is 52,040 Calories per kg-mol of H_2SO_4 formed.

H_2SO_4 formed in chambers = 1.19 kg-mols.

Heat evolved = $1.19 \times 52,040 = \dots\dots\dots$ 62,000 Calories

2. Heat evolved in dissolving H_2SO_4 . Integral heat of solution (Fig. 54) at a concentration of 64% H_2SO_4 = 11,800 Calories per kg-mol.

Heat evolved in dissolution = $11,800 \times 1.19 = \dots\dots\dots$ 14,030 Calories

3. Heat content of dry gases and water vapor entering. This has already been calculated as part of the heat output of the Glover tower = $\dots\dots\dots$ 29,120 Calories

4. Heat content of spray water. Since the spray water enters at the reference temperature, 18° C, its heat content is equal to $\dots\dots\dots$ 0 Calories

5. Heat content of dry gases leaving. Mean heat capacity between 18° and 40° C (from Fig. 12).

SO_2 $0.021 \times 9.15 = \dots\dots\dots$ 0.19 Calories per °C

$\text{O}_2, \text{N}_2, \text{NO}$ $14.98 \times 6.95 = \dots\dots\dots$ 104 Calories per °C

Total heat capacity = $\dots\dots\dots$ 104.2 Calories per °C

Total heat content of dry gases = $104.2(40 - 18) = \dots\dots\dots$ 2300 Calories

6. Heat content of water vapor leaving.

Dew-point = 8° C.

Heat of vaporization at 8° C (Fig. 10) = 10,650 Calories per kg-mol.

Total heat content =

$0.167[10,640 - 18(18 - 8) + 8.4(40 - 18)] = \dots\dots\dots$ 1800 Calories

7. Heat absorbed in cooling the acid leaving. Heat capacity (Fig. 55) of acid containing 64% H_2SO_4 = 0.50 Calories per kg per °C.

Heat content = $0.50 \times 182(68 - 25) = \dots\dots\dots$ 3920 Calories

8. Heat content of acid leaving the cooler =

$0.50 \times 182(25 - 18) = \dots\dots\dots$ 640 Calories

Summary of Heat Balance of Chambers.

<i>Input</i>		
Heat content of dry gases from Glover tower...	8,720 Calories	8.3%
Heat content of water vapor in gases entering...	20,400 Calories	19.4%
Heat content of spray water.....	0 Calories	0%
Heat evolved in forming H_2SO_4	62,000 Calories	59.0%
Heat evolved in dissolving H_2SO_4	14,030 Calories	13.3%
Total.....	105,150 Calories	100.0%

<i>Output</i>		
Heat content of dry gases leaving.....	2,300 Calories	2.2%
Heat content of water vapor in gases.....	1,800 Calories	1.7%
Heat content of acid leaving the cooler.....	640 Calories	0.6%
Heat absorbed by cooler.....	3,920 Calories	3.7%
Heat loss from chambers (by difference).....	96,490 Calories	91.8%
Total.....	105,150 Calories	100.0%

This heat balance is presented diagrammatically in Fig. 58.

It will be seen that nearly the entire source of heat energy (72.3%) comes from the formation of H_2SO_4 and its dilution whereas nearly the entire heat input is lost by radiation from the very extensive lead surfaces of the chambers. More recent developments in the chamber process have provided for more rapid means of heat removal with much less floor space and size of equipment by rapid circulation of both gases and acid in packed towers.

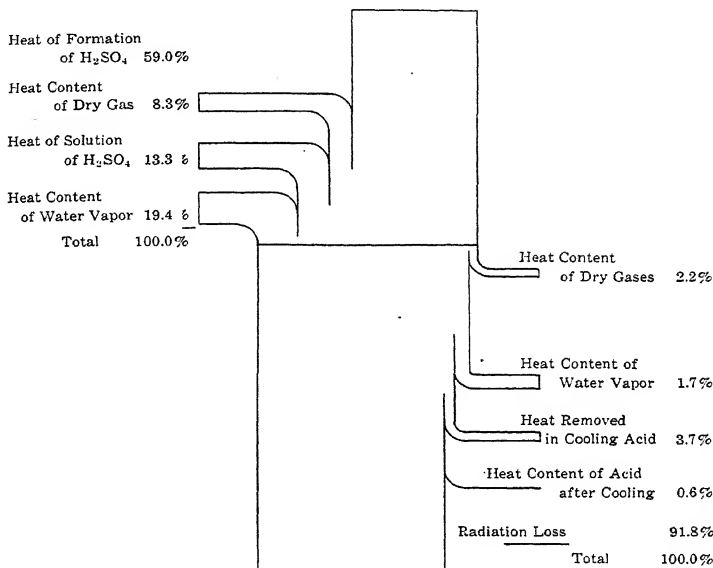


FIG. 58. Heat Balance of Chambers.

WEIGHT BALANCE OF GAY-LUSSAC TOWER

The purpose of the Gay-Lussac tower is to recover the oxides of nitrogen from the chamber gases. These oxides are then returned to the system in the Glover tower. The water remaining in the chamber gases is also absorbed. The conditions favorable for absorption of the oxides of nitrogen are a high concentration of acid, a low temperature, and a low concentration of SO_2 in the residual gas. A high water content in the gas from the chambers causes objectionable dilution of the acid. Small amounts of SO_2 will cause decomposition of nitrosyl-sulphuric acid with release and loss of the oxides of nitrogen. The presence of oxygen is essential to effect the oxidation of NO to N_2O_3 and its absorption in the acid.

The loss of oxides of nitrogen in the gases from the Gay-Lussac tower may be assumed to be equivalent to the make-up nitric acid introduced. It will be assumed that these oxides leave in the form of NO .

1. Input. The input to the Gay-Lussac tower consists of the wet gases from the

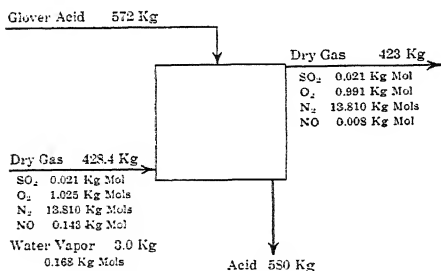
chambers and the Glover acid which is introduced. All the gases pass through the tower unchanged with the exception of the NO and O_2 .

2. NO in gas leaving = $0.008 \text{ kg-mol} = \dots\dots\dots 0.2 \text{ kg}$
 3. O_2 in gases leaving:
 NO oxidized to $\text{N}_2\text{O}_3 = 0.143 - 0.008 = \dots\dots\dots 0.135 \text{ kg-mol}$
 O_2 consumed = $0.135/4 = \dots\dots\dots 0.034 \text{ kg-mol}$
 O_2 leaving = $1.025 - 0.034 = 0.991 \text{ kg-mol} = \dots\dots 31.7 \text{ kg}$

Summary of Weight Balance of Gay-Lussac Tower.

Input		Output	
SO_2 (0.021 kg-mol)	1.3 kg	SO_2 (0.021 kg-mol)	1.3 kg
O_2 (1.025 kg-mols)	32.8 kg	O_2 (0.991 kg-mol)	31.7 kg
N_2 (13.81 kg-mols)	390.0 kg	N_2 (13.81 kg-mols)	390.0 kg
NO (0.143 kg-mol)	4.3 kg	Acid leaving	580.0 kg
H_2O (0.168 kg-mol)	3.0 kg	NO (0.008 kg-mol)	0.2 kg
Glover acid	572.0 kg		
Total	1003.4 kg	Total	1003.2 kg

This weight balance is summarized diagrammatically in Fig. 59.



HEAT BALANCE OF GAY-LUSSAC TOWER

1. Heat evolved in forming and dissolving N_2O_3 . The N_2O_3 released from the Gay-Lussac acid and decomposed in the Glover tower is reformed and recovered in the Gay-Lussac tower evolving 3440 Calories calculated as part of the heat balance of the Glover tower, page 299.

FIG. 59. Weight Balance of Gay-Lussac Tower.

2. Heat evolved in the dissolution of the water vapor absorbed. The water vapor leaving the last chamber is completely absorbed in the Gay-Lussac tower. Since the resulting concentration change in this absorption is negligible, it is necessary to determine the heat evolved in the dissolution of the water from data on the partial heat of solution of water in sulphuric acid solutions. From Fig. 54, the partial molal heat of solution of water in a sulphuric acid solution containing 77.7% H_2SO_4 is 3100 Calories per kg-mol. This value neglects the effect of the dissolved oxides of nitrogen.

Heat evolved = $3100 \times 0.167 = \dots\dots\dots 520 \text{ Calories}$

3. Heat content of Glover acid introduced.

Heat capacity (Fig. 55) = 0.44 Calories per kg per $^{\circ}\text{C}$.

Heat content = $572 \times 0.44(25 - 18) = \dots\dots\dots$

1750 Calories

4. Heat content of entering gases. Already calculated as output items in the heat balance of the chambers = 4100 Calories

5. Heat content of gases leaving. Mean heat capacity between 18° C and 30° C (from Fig. 12).

$$\text{SO}_2 = 0.021 \times 9.1 = \dots\dots\dots 0.19 \text{ Calories per } ^\circ\text{C}$$

$$\text{O}_2, \text{NO}, \text{N}_2 = 14.81 \times 6.95 = \dots\dots\dots 102.9 \text{ Calories per } ^\circ\text{C}$$

$$\text{Total} = \dots\dots\dots 103.1 \text{ Calories per } ^\circ\text{C}$$

$$\text{Heat content} = 103(30 - 18) = \dots\dots\dots 1235 \text{ Calories}$$

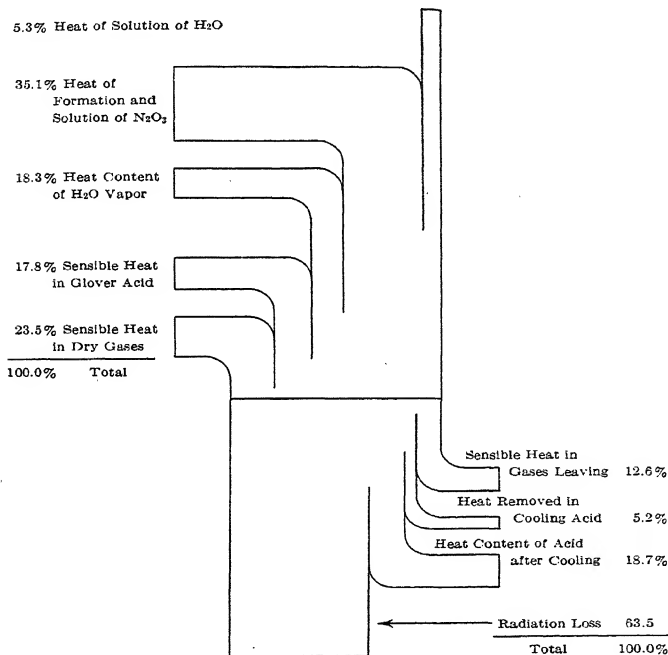


FIG. 60. Heat Balance of Gay-Lussac Tower.

6. Heat absorbed in cooling acid.

$$580 \times 0.45(27 - 25) = \dots\dots\dots 510 \text{ Calories}$$

7. Heat content of acid leaving cooler.

$$580 \times 0.45(25 - 18) = \dots\dots\dots 1830 \text{ Calories}$$

Summary of Heat Balance of Gay-Lussac Tower.

<i>Input</i>		
Heat content of dry gases entering =	2,300 Calories	23.5%
Heat content of water vapor entering =	1,800 Calories	18.3%
Heat content of Glover acid entering =	1,750 Calories	17.8%
Heat evolved in forming N_2O_3 =	1,480 Calories	15.1%
Heat evolved in dissolving N_2O_3 =	1,960 Calories	20.0%
Heat evolved in dissolving H_2O =	520 Calories	5.3%
Total =	9,810 Calories	100.0%

<i>Output</i>		
Heat content of gases leaving =	1,235 Calories	12.6%
Heat absorbed in cooling acid =	510 Calories	5.2%
Heat content of acid leaving cooler =	1,830 Calories	18.7%
Heat loss (by difference) =	6,235 Calories	63.5%
Total =	9,810 Calories	100.0%

This heat balance is shown diagrammatically in Fig. 60.

SUMMARIZED HEAT BALANCE FOR ENTIRE PLANT

Reference temperature: 18° C.

Basis: 100 kg of dry pyrites charged.

<i>Input</i>		
1. Heat of combustion of pyrites =	143,400 Calories	61.4%
2. Heat content of water vapor in air =	1,850 Calories	0.8%
3. Heat evolved in formation of H_2SO_4 in Glover tower	11,950 Calories	5.1%
4. Sensible heat content of nitric acid	7 Calories	0.0%
5. Heat evolved in formation of H_2SO_4 in chamber	62,000 Calories	26.5%
6. Heat evolved in solution of H_2SO_4 in chamber	14,030 Calories	6.0%
7. Solution of H_2O in Gay-Lussac tower	520 Calories	0.2%
Total	233,757 Calories	100.0%

<i>Output</i>		
1. Heat in cinders	5,540 Calories	2.4%
2. Net heat of concentrating acid in Glover tower	2,400 Calories	1.0%
3. Concentration and decomposition of nitric acid	276 Calories	0.1%
4. Radiation losses from burners	81,540 Calories	34.9%
Radiation losses from Glover tower	2,061 Calories	0.9%
Radiation losses from chamber	96,490 Calories	41.3%
Radiation losses from Gay-Lussac tower	6,235 Calories	2.7%

5. Cooling losses — Glover acid.....	33,000 Calories	14.1%
Cooling losses — chamber acid.....	3,920 Calories	1.7%
Cooling losses — Gay-Lussac acid.....	510 Calories	0.2%
6. Heat content of acid product 178 (0.44) (25 — 18).....	550 Calories	0.2%
7. Heat content of spent gases leaving Gay- Lussac tower.....	1,235 Calories	0.5%
Total.....	233,757 Calories	100.0%

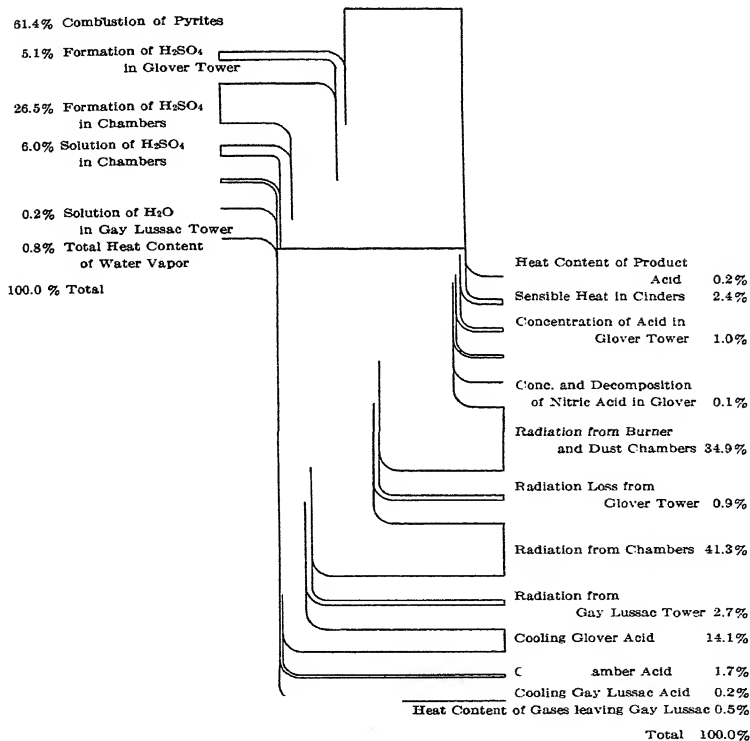


FIG. 61. Heat Balance of an Entire Sulphuric Acid Plant.

The heat balance for the entire sulphuric acid plant is shown diagrammatically in Fig. 61.

THE WEIGHT AND HEAT BALANCES OF A BLAST FURNACE

A blast furnace is essentially a huge gas producer where, in conjunction with the partial combustion and distillation of a carbonaceous fuel, the reduction of ore and the formation of slag occur simultaneously. The charge, consisting of iron ore, coke, and limestone in proper proportions, is fed into the top of the blast furnace. Preheated air, preferably free from water vapor, is blown through the tuyères near the bottom of the furnace into the descending stream of solids resulting in combustion of the coke present to carbon dioxide. The carbon dioxide gas in the presence of excess coke is reduced at the high prevailing temperature to carbon monoxide. A great many chemical reactions occur within the furnace. As the charge descends the shaft and as its temperature is gradually increased, dehydration of the ore, coke, and limestone takes place, followed by distillation of the remaining volatile matter of the coke, calcination of magnesium and calcium carbonates present in the limestone or ore, and reduction of the higher oxides of manganese and iron to manganous and ferrous oxides by the rising stream of reducing gases. The carbon dioxide formed by reduction of the ore with carbon monoxide is reduced in the presence of excess coke. As the temperature of the descending charge becomes still higher the lower oxides of iron and manganese are reduced to the metallic state.

At the highest temperature of the tuyères, part of the silica present is reduced to the metallic state and is dissolved in the molten iron. The excess silica and alumina of the charge are fluxed by reaction with the metallic bases present resulting in the formation of a fusible slag consisting of complex silicates and aluminates of calcium, magnesium, and iron. The high temperature at the tuyères produces a fluid slag and molten metal which readily flow through the solid reacting charge, separate into two layers at the bottom of the furnace, and are periodically run out in two separate streams as molten pig iron and as molten slag. A high temperature at the tuyères favors a ready separation of the slag and removal, as CaS in the slag, of much sulphur which was originally present in the coke. The temperature of the blast furnace is too low and insufficient coke is present to reduce the oxides of calcium, magnesium, and aluminum and the silicates. Hence, these compounds pass into the slag. Silica is used as a flux in a few exceptional cases where the alkaline earths and alumina predominate in the gangue present in the ore.

The purpose of preheating the air used in combustion of the coke is to permit the attainment of the high temperatures necessary for the final reduction of the ore and the fusion of the pig iron and slag. Any water vapor present in the incoming air will lower the temperature in the

fusion zone on account of the heat absorbed in its reduction to hydrogen and carbon monoxide. For this reason it is desirable to use a blast of dried air.

The products of the blast furnace consist of molten pig iron, slag, and blast-furnace gas. The outgoing gas consists essentially of nitrogen carbon monoxide, carbon dioxide, and water vapor, with small amounts of hydrogen and methane, and also carries in suspension a considerable amount of dust. The heating value of this gas is very low because of its high content of nitrogen and the small amount of volatile matter in the coke which is used for reduction. The free moisture in the incoming charge is distilled off near the top of the furnace and escapes into the blast furnace gas without reduction.

The slag contains all the lime, magnesia, alumina, and alkalies originally present in the ore and flux, together with most of the silica and some ferrous and manganous oxides. The exact mineralogical compositions of ore, flux, and slag are usually not known completely, so that some uncertainty exists concerning the exact thermal energy involved in reduction and chemical transformations. The molten pig iron contains, in addition to iron, some carbon present as cementite and lesser amounts of silicon and manganese. On cooling, the cementite partly decomposes into graphite and iron.

In order to establish the weight balance of a blast furnace it is necessary to know the weights and chemical compositions of the ore, flux, dust, and pig iron and the analysis of the dry blast-furnace gas. The weights of slag, air, and water vapor can then be calculated.

The weight balance includes:

<i>Input</i>	<i>Output</i>
Iron ore	Dry gases
Flux	Water vapor in gases
Coke	Pig iron
Air	Dust
Water vapor	Slag

As an illustration of the calculations involved in the weight and heat balance of a blast furnace, the data for the reduction of a basic iron ore with charcoal and an acid flux will be given. An example of the more usual operation with a limestone flux is given in the problems at the end of this chapter. The balances are worked out on a basis of 100 kilograms of pig iron produced.

Illustration 2. A blast furnace is charged with 212.7 kg of ore, 110.0 kg of charcoal, and 13.9 kg of flux per 100 kg of pig iron produced. The compositions of these materials are as follows:

Ore (212.7 kg)		Charcoal (110.0 kg)	
Fe ₂ O ₃	54.93%	C.....	86.89%
FeO...	8.48%	O.....	3.15%
CaO...	9.58%	H.....	0.45%
Mn ₂ O ₄ ...	4.97%	N.....	0.51%
Al ₂ O ₃ ...	3.00%	H ₂ O.....	7.00%
MgO...	1.83%	Ash.....	2.00%
SiO ₂ ...	4.92%		
	4.48%		100.00%
CO ₂ ...	7.81%		
	100.00%		
Flux (13.9 kg)		Pig Iron (100.0 kg)	
SiO ₂	78.38%	C.....	3.12%
Al ₂ O ₃	13.99%	Si.....	1.52%
CaO.....	0.53%	Mn.....	2.22%
Fe ₂ O ₃	3.90%	Fe.....	93.14%
H ₂ O.....	3.20%		
	100.00%		100.00%

The total heating value of the charcoal is 7035 Calories per kg.

The clean gas produced has the following composition by volume on the moisture free basis:

CO ₂	12.62%
CO.....	25.56%
CH ₄	0.69%
H ₂	1.34%
N ₂	59.79%
	<hr/> 100.00%

The ore, flux, and charcoal are charged to the furnace at an average temperature of 18° C. The air blast is dried and enters the tuyères at a temperature of 300° C and moisture-free.

The gases leave the furnace at a temperature of 173° C and contain only negligible quantities of dust.

The slag and pig iron are poured at an average temperature of 1360° C.

In order to cool the outside of the bosh of the furnace and thereby protect the refractories from excessive heating, water is circulated in a pipe passing around the circumference of the bosh. On the basis of 100 kg of pig iron produced 576 kg of water are circulated and heated through a temperature rise of 13° C.

Calculate the complete weight and heat balances of this furnace.

WEIGHT BALANCE

Distribution of Ore Materials. The mineralogical composition of the ore is not given, although it is customary to assume that the carbon dioxide present is combined with the lime and the magnesia present as limestone. This limestone is calcined at about 900° C to CaO, MgO, and CO₂. The silica is present chiefly as silicates of aluminum and magnesium. Any free moisture present in the ore is driven off at the top of the furnace without reduction. However, the chemically combined water,

as in the minerals kaolinite and limonite, will be retained until the ore reaches a hotter zone, where it will be partly reduced by coke to hydrogen and carbon monoxide. It will be assumed that all the elements of the carbon dioxide and water of the ore leave the blast furnace in the gases.

The alumina, lime, and magnesia pass into the slag without reduction but combine with the silica of the flux to form complex silicates of calcium, magnesium, and aluminum. The exact thermal energy of this latter change is unknown since the mineralogical composition of the slag as well as the heats of formation of complex silicates are unknown.

The higher oxides of iron are reduced at a relatively low temperature to the lower oxides, and finally in the hot zone of the furnace sufficient is reduced to the metallic state to supply the iron requirements of the pig iron. It is assumed that the remaining iron, as ferrous oxide, passes into the slag forming ferrous silicate. This assumption is somewhat inexact because it is known that a part of the iron exists as metallic particles included in the slag.

Sufficient silica is reduced to metallic silicon to supply the silicon content of the pig iron. The remainder combines with the basic oxides to form silicates in the slag.

The Mn_2O_4 of the ore is in part reduced to metallic manganese, supplying that present in the pig iron. The remainder of the manganese is assumed to enter the slag as MnO , forming silicates.

The oxygen given up in the reduction of the oxides of iron, silicon, and manganese will be present in the gases as CO or CO_2 or H_2O . The gases also contain the CO_2 and H_2O of the ore, in partly reduced forms.

Basis: 100 kg of pig iron produced.

Distribution of Fe_2O_3 and FeO .

Fe_2O_3 in ore = $212.7 \times 0.5493 = 116.8$ kg or $\frac{116.8}{159.7} = \dots$	0.732 kg-mol
FeO in ore = $212.7 \times 0.0848 = 18.03$ kg or $\frac{18.03}{71.8} = \dots$	0.2515 kg-mol
Total Fe in ore = $2 \times 0.732 + 0.2515 = \dots$	1.7155 kg-atoms
Fe in pig iron = 93.14 kg or $\frac{93.14}{55.8} = \dots$	1.669 kg-atoms
Fe into slag as $FeO = \dots$	0.0465 kg-atom
FeO into slag = 0.0465 kg-mol or $0.0465 \times 71.8 = \dots$	3.33 kg
Oxygen in iron oxides of ore = $(3/2 \times 0.732)$ + $(\frac{1}{2} \times 0.2515) = \dots$	1.223 kg-mols
Oxygen in FeO of slag = $\frac{1}{2} \times 0.0465 = \dots$	0.023 kg-mol
Oxygen into gases = \dots	1.20 kg-mols
or $1.20 \times 32 = \dots$	38.4 kg

Distribution of SiO_2 .

SiO_2 in ore = $212.7 \times 0.0492 = 10.47$ kg or $\frac{10.47}{60.1} = \dots$	0.174 kg-mol
Si in pig iron = 1.52 kg or $\frac{1.52}{28.1} = \dots$	0.054 kg-atom
Si into slag as $SiO_2 = \dots$	0.120 kg-atom
SiO_2 into slag = 0.120 kg-mol or $0.120 \times 60.1 = \dots$	7.2 kg
O_2 into gases = 0.054 kg-mol or $0.054 \times 32 = \dots$	1.7 kg

Distribution of Mn_2O_3 .

Mn_2O_3 in ore = $212.7 \times 0.0497 = 10.57$ kg or $\frac{10.57}{228.8} =$	0.0462 kg-mol
Mn in ore = $0.0462 \times 3 =$	0.1386 kg-atom
Mn in pig iron = 2.22 kg or $\frac{2.22}{54.9} =$	0.0405 kg-atom
Mn into slag =	0.0981 kg-atom
MnO into slag = 0.0981 kg-mol or $0.0981 \times 70.9 =$	6.95 kg
Oxygen in Mn_2O_3 of ore = $2 \times 0.0462 =$	0.0924 kg-mol
Oxygen in MnO of slag = $\frac{1}{2} \times 0.0981 =$	0.0491 kg-mol
Oxygen into gases =	0.0433 kg-mol
or $0.0433 \times 32 =$	1.38 kg

Distribution of H_2O and CO_2 .

Both compounds enter the gases in partly reduced forms.

H_2O in ore = $212.7 \times 0.0448 = 9.52$ kg or $\frac{9.52}{18.02} =$	0.529 kg-mol
CO_2 in ore = $212.7 \times 0.0781 = 16.62$ kg or $\frac{16.62}{44} =$	0.378 kg-mol
H_2 into gases = 0.529 kg-mol or $0.529 \times 2.02 =$	1.06 kg
C into gases = 0.378 kg-atom or $0.378 \times 12 =$	4.54 kg
Total O_2 into gases = $0.378 + (\frac{1}{2} \times 0.529) = 0.642$ kg-mol or	20.54 kg

Summary of distribution of ore materials.

Into pig iron:

Fe =	93.14 kg
Mn =	2.22 kg
Si =	1.52 kg

Into slag:

FeO =	3.33 kg
$\text{SiO}_2 =$	7.2 kg
MnO =	6.95 kg
$\text{CaO} = 212.7 \times 0.0958 =$	20.4 kg
$\text{Al}_2\text{O}_3 = 212.7 \times 0.0300 =$	6.4 kg
$\text{MgO} = 212.7 \times 0.0183 =$	3.9 kg

Into gases:

O = $38.4 + 1.7 + 1.38 + 20.54 =$	62.0 kg
C =	4.54 kg
H =	1.06 kg

Total = 212.6 kg

Distribution of Flux Materials. Since it has been assumed in the preceding calculations that all the iron, manganese, and silicon of the pig iron were derived from the ore materials, all the materials of the flux must pass into the slag or the gases. The silica, lime, and alumina enter the slag unchanged. It will be assumed that the ferric oxide is reduced to FeO and enters the slag in this form. The oxygen evolved in the reduction of the iron oxide and the water present in the flux enter the gases.

Basis: 100 kg of pig iron produced.

Distribution of iron oxide.

Fe_2O_3 in flux = $13.9 \times 0.0390 = 0.542$ kg or.....	0.0034 kg-mol
FeO into slag = $2 \times 0.0034 = 0.0068$ kg-mol or.....	0.49 kg
O_2 into gases = $\frac{1}{2} \times 0.0034 = 0.0017$ kg-mol or.....	0.05 kg

Distribution of water.

H_2O in flux = $13.9 \times 0.0320 = 0.445$ kg or.....	0.0247 kg-mol
H_2 into gases = 0.0247 kg-mol or.....	0.05 kg
O_2 into gases = $\frac{1}{2} \times 0.0247 = 0.0123$ kg-mol or.....	0.39 kg

Summary of distribution of flux materials.

Into slag:

$\text{SiO}_2 = 13.9 \times 0.7838 =$	10.90 kg
$\text{Al}_2\text{O}_3 = 13.9 \times 0.1399 =$	1.95 kg
$\text{CaO} = 13.9 \times 0.0053 =$	0.07 kg
$\text{FeO} =$	0.49 kg

Into gases:

$\text{O} = 0.05 + 0.39 =$	0.44 kg
$\text{H} =$	0.05 kg
Total =	13.90 kg

Distribution of Charcoal. The carbon in the pig iron will be assumed to be derived from the charcoal. The ash will enter the slag while the remainder of the charcoal constituents will pass into the gases.

Distribution of water.

H_2O in charcoal = $110.0 \times 0.0700 = 7.70$ kg or.....	0.428 kg-mol
H_2 into gases = 0.428 kg-mol or.....	0.86 kg
O_2 into gases = 0.214 kg-mol or.....	6.85 kg

Summary of distribution of charcoal materials.

Into pig iron:

$\text{C} =$	3.12 kg
--------------------	---------

Into gases:

$\text{C} = (110.0 \times 0.8689) - 3.12 =$	92.44 kg
$\text{H} = (110.0 \times 0.0045) + 0.86 =$	1.36 kg
$\text{O} = (110.0 \times 0.0315) + 6.85 =$	10.32 kg
$\text{N} = 110.0 \times 0.0051 =$	0.56 kg

Into slag:

Ash = $100.0 \times 0.02 =$	2.20 kg
Total =	110.00 kg

Weight and Composition of Slag. Since it may be assumed that the slag contains only materials derived from the ore, flux, and charcoal, its total weight and composition may be obtained by adding together the weights of materials entering the slag from these three sources. Actually these materials will be in the slag in the form of complex compounds.

<i>Component</i>	<i>Weight, kg</i>	<i>Percentage</i>	<i>Kg equivalents</i>
FeO = $3.33 + 0.49 = \dots$	3.82	6.0	0.106
SiO ₂ = $7.2 + 10.90 = \dots$	18.10	28.4	0.608
MnO = $\dots\dots\dots$	6.95	10.9	0.196
CaO = $20.4 + 0.07 = \dots$	20.47	32.1	0.730
Al ₂ O ₃ = $6.4 + 1.95 = \dots$	8.35	13.1	0.164
MgO = $\dots\dots\dots$	3.90	6.1	0.320
Ash = $\dots\dots\dots$	2.20	3.4	
Total = $\dots\dots\dots$	63.79 kg	100.0%	

In calculating the kilogram equivalents, alumina is assumed to behave as an acid. Neglecting the charcoal ash:

Total kilogram equivalents of metallic bases = 1.352.

Total kilogram equivalents of acids (SiO₂ and Al₂O₃) = 0.772.

It is apparent that the slag is distinctly basic in character, despite the fact that an acid flux was used.

In order to verify the above calculations it is possible to determine the weight and composition of the slag experimentally.

Weight of Dry, Clean Blast Furnace Gas. The direct measurement of the volume of blast furnace gas is difficult and rarely undertaken. The volume or weight of gases can be calculated from a carbon balance as in obtaining the weight balance of a combustion process. The carbon in the blast furnace gas comes from the carbon dioxide of the limestone of the ore and from the charcoal used for reduction.

Carbon Balance.

Basis: 100 kg of pig iron produced.

Total C into gases = $4.54 + 92.44 = 96.98$ kg or 8.08 kg-atoms

Carbon per kg-mol of dry, clean gas (from gas analysis) =

$0.1262 + 0.2556 + 0.0069 = \dots\dots\dots$ 0.3887 kg-atom

Total dry gas = $8.08/0.3887 = \dots\dots\dots$ 20.78 kg-mols

CO₂ = $20.78 \times 0.1262 = 2.62$ kg-mols or $\times 44 = \dots$ 115.2 kg

CO = $20.78 \times 0.2556 = 5.30$ kg-mols or $\times 28 = \dots$ 148.3 kg

CH₄ = $20.78 \times 0.0069 = 0.14$ kg-mol or $\times 16 = \dots$ 2.2 kg

H₂ = $20.78 \times 0.0134 = 0.28$ kg-mol or $\times 2.02 = \dots$ 0.57 kg

N₂ = $20.78 \times 0.5979 = 12.44$ kg-mols or $\times 28.2 = \dots$ 351.5 kg

Total = $\dots\dots\dots$ 20.78 kg-mols or $\dots\dots\dots$ 617.8 kg

Average molecular weight = $617.8/20.78 = 29.7$.

Weight of Air Introduced. The weight of dry air introduced is calculated from a nitrogen balance as in the case of a combustion process. The nitrogen in the gas is derived from only two sources, the charcoal and the air.

N₂ in gases = $\dots\dots\dots$ 351.5 kg

N₂ from charcoal = $\dots\dots\dots$ 0.56 kg

N₂ from air = $\dots\dots\dots$ 350.9 kg or 12.42 kg-mols

Air introduced = $12.42/0.79 = \dots\dots\dots$ 15.72 kg-mols

or $15.72 \times 29.0 = \dots\dots\dots$ 456 kg

Since the air is dried, containing no water vapor, this is the total weight of the air introduced.

: of Water Vapor in Blast Furnace Gas. The weight of water vapor in the blast furnace gas is calculated from a hydrogen balance. All hydrogen of the entering materials is present in the gas either as H_2 , CH_4 , or H_2O .

Basis: 100 kg of pig iron produced.

Total H introduced = $1.06 + 0.05 + 1.36 = 2.47$ kg.

Output of H.

As $H_2 = \dots\dots\dots 0.57$ kg

As $CH_4 = 2 \times 0.14 \times 2.02 = \dots\dots\dots 0.57$ kg

Total = $\dots\dots\dots 1.14$ kg

As $H_2O = 2.47 - 1.14 = 1.33$ kg or $\dots\dots\dots 0.66$ kg-mol

H_2O in gases = 0.66 kg-mol or $\dots\dots\dots 11.9$ kg

H_2O introduced in charge = $9.52 + 0.44 + 7.70 = \dots\dots\dots 17.66$ kg

H_2O decomposed in blast furnace = $17.66 - 11.9 = \dots\dots\dots 5.76$ kg

or $5.76/18 = \dots\dots\dots 0.320$ kg-mol

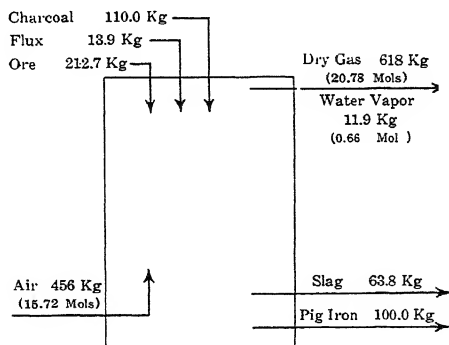


FIG. 62. Weight Balance of a Blast Furnace.

Complete Weight Balance.

Input		Output	
Ore.....	212.7 kg	Slag.....	63.8 kg
Flux.....	13.9 kg	Dry gas (20.78 kg-mols).....	617.8 kg
Charcoal.....	110.0 kg	Water vapor in gas (0.66 kg-mol)....	11.9 kg
Air (15.72 kg-mols)	456.0 kg	Pig iron.....	100.0 kg
Total.....	792.6 kg	Total.....	793.5 kg

This weight balance is summarized diagrammatically in Fig. 62.

HEAT BALANCE

A heat balance might be established by considering the relative heat contents and heats of formation of all components of the charge and all components of the slag, pig iron, and furnace gas together with the heat loss by radiation. Such a heat balance would be disproportionate since the chemical energies of formation of the oxides and silicates which pass through the process unchanged, such as the oxides of aluminum, silicon, calcium, and magnesium, are of no interest. More valuable information is obtained by including in the heat balance only the *net* chemical and thermal changes which take place during the process.

During the course of reduction many intermediate chemical reactions take place each accompanied by a certain thermal change. Examples are the progressive reduction of the higher oxides of iron and manganese, the oxidation of carbon at the tuyères and its subsequent reduction by coke to carbon monoxide, the reduction of metallic oxides by carbon and by carbon monoxide, and the reduction of water to carbon monoxide, hydrogen, and carbon dioxide. However, in any chemical process the total change in energy is dependent only upon the initial and final states of chemical constitution, temperature, pressure, and state of aggregation and is independent of any intermediate state. Hence, in calculating the heat balance of a blast furnace, the numerous intermediate reactions involved need not be considered. It is sufficient to know the temperature, state of aggregation, and composition of each material charged and each product formed, without knowing how the various components of the products are actually produced.

The oxides of calcium, magnesium, and aluminum pass through the furnace apparently unchanged so that the heats of formation of these oxides need not be considered, but the state of the oxide is much different in the slag from that in the ore or flux. For example, in the ore, the oxides of iron and manganese exist as oxides but in the slag as silicates, so that the net heat effect accompanying the formation of silicates from the oxides should be considered. However, accurate calculation of this quantity requires data which are not ordinarily available.

The heat balance will be calculated with a reference temperature of 18° C, based on 100 kg of pig iron produced.

1. *Heat of reduction of iron oxides.* The heat evolved is obtained by subtracting the total heat of formation of the reactants from that of the products. Iron oxides enter the process in both the ore and the flux. The necessary heat of formation data are obtained from Table X, page 159.

<i>Reactants</i>	<i>Kg-mols</i>	<i>Molal Heat of Formation</i>	<i>Total Heat of Formation, Calories</i>
Fe ₂ O ₃	0.735	191,600	141,100
FeO	0.2515	64,000	16,100
Total =			157,200 Calories
<i>Products</i>			
Fe	1.669	0	
FeO	0.0533	64,000	3,400
Oxygen	1.25	0	
Heat evolved in reduction of iron oxides = 3400 -			
157,200 =			-153,800 Calories

2. Heat of reduction of Mn_2O_4 .

<i>Reactant</i>	<i>Kg-mols</i>	<i>Molal Heat of Formation</i>	<i>Total Heat of Formation, Calories</i>
Mn_2O_4	0.0462	328,000	15,150
<i>Products</i>			
Mn	0.0405	0	
MnO	0.0981	90,800	8,910
Oxygen	0.0433	0	

Heat evolved in reduction of $Mn_2O_4 = 8910 - 15,150 = -6240$ Calories

3. Heat of reduction of SiO_2 .

<i>Reactant</i>	<i>Kg-mols</i>	<i>Molal Heat of Formation</i>	<i>Total Heat of Formation, Calories</i>
SiO_2 reduced	0.054	201,000	10,850
<i>Products</i>			
Si	0.054	0	
O	0.054	0	

Heat evolved in reduction of $SiO_2 = \dots\dots\dots -10,850$ Calories

4. Heat of calcination of carbonates. Carbonates are present only in the ore. It is assumed that all CaO of the ore is combined with CO_2 as the carbonate and that the surplus CO_2 is combined with MgO.

CO_2 in ore =	0.378 kg-mol
CaO in ore = $20.4/56 =$	0.364 kg-mol
MgO in ore = $3.9/40.3 =$	0.096 kg-mol
$CaCO_3$ in ore =	0.364 kg-mol
$MgCO_3$ in ore = $0.378 - 0.364 =$	0.014 kg-mol
MgO in ore = $0.096 - 0.014 =$	0.082 kg-mol

<i>Reactant</i>	<i>Kg-mols</i>	<i>Molal Heat of Formation</i>	<i>Total Heat of Formation, Calories</i>
$CaCO_3$	0.364	288,000	104,900
$MgCO_3$	0.014	267,500	3,740
Total =			108,640 Calories
<i>Products</i>			
CO_2	0.378	94,400	35,650
CaO	0.364	151,700	55,200
MgO	0.014	145,600	2,020

Total = $\dots\dots\dots 92,870$ Calories

Heat evolved in calcination = $92,870 - 108,640 = \dots\dots -15,770$ Calories

5. Heat of partial combustion of charcoal. The purpose of introducing charcoal into the charge is to furnish heat for all endothermic reactions involved in reduction, to supply heat for producing the slag and pig iron in a molten state, and to supply carbon for the reduction of the various metallic oxides of the ore. The charcoal is not burned completely to carbon dioxide and water vapor, and its total heating value

is not rendered available in the blast furnace. The actual products resulting from the partial combustion of the charcoal include carbon dioxide, water vapor, carbon monoxide, methane, and hydrogen in the outgoing gases and graphite in the solidified pig iron.

Since the heats of formation of the materials making up the charcoal are not known it is necessary to calculate the heat evolved in its partial combustion from standard heat of combustion data. As pointed out in Chapter VI, page 173 the heat evolved in a reaction is the difference between the sum of the heats of combustion of the reactants and that of the products. The actual reactants entering into the combustion of the charcoal include carbon dioxide, water vapor, and oxygen from both the air and the ore. However, the heats of combustion of these materials are zero, and they need not be considered in calculating the heat of reaction. Since all the combustible components of the gases must originate from the reactions of the charcoal, it is not necessary to consider the intermediate course of the reaction.

Heat of combustion of reactant, charcoal, = $110.0 \times 7035 = \dots$ 773,800 Calories

Product	Kg-mols	Molal Heat of Combustion	Total Heat of Combustion, Calories
CO	5.30	67,620	358,500
CH ₄	0.14	212,790	29,800
H ₂	0.28	68,310	19,100
Graphite = 3.12/12	0.26	94,400	24,500
Total			431,900 Calories

Heat evolved in partial combustion of charcoal = 773,800
 - 431,900 = 341,900 Calories

6. Heat evolved in formation of slag. Blast-furnace slags consist of complex mixtures of silicates and aluminates of calcium, magnesium, iron, and manganese. In order to calculate the heat of reaction accompanying the formation of a slag it would be necessary to determine the complete mineralogical composition of the ore, flux, and slag, together with the heats of formation of all the compounds present. Such data are rarely available, and it is ordinarily necessary to neglect the heat evolved in forming the slag from the oxides. It would not be expected that this thermal effect is large. The formation of the monosilicate of calcium, manganese, iron, or magnesium from SiO₂ and the respective oxide is in every case accompanied by an evolution of heat. On the other hand, the formation of dicalcium silicate is accompanied by an absorption of heat. These effects will frequently tend to compensate each other.

7. Heat absorbed in the formation of cementite. In the blast furnace some carbon combines with iron to form cementite, Fe₃C, with simultaneous absorption of heat. The formation of cementite is an endothermic reaction requiring 4000 kg calories per kg-mol of Fe₃C. Upon slow cooling of pig iron this cementite is partly decomposed with liberation of heat. In this instance the carbon present in the pig iron is assumed to remain present as cementite because of rapid cooling during solidification.

Heat absorbed in formation of cementite = $4000 \times \frac{3.12}{12} = \dots$ 1,040 Calories

This item of heat absorbed is neglected in the output of the present heat balance.

8. Heat content of air.

Air supplied = 15.72 kg-mol.

Mean molal heat capacity between 18° C and 300° C (from Fig. 12, page 116) = 7.03 Calories per °C.

$$\text{Heat content of air} = 15.72 \times 7.03(300 - 18) = \dots \quad 31,200 \text{ Calories}$$

9. Heat content of dry blast-furnace gas.

Mean heat capacity between 18° C and 173° C (from Fig. 12).

CO ₂	2.62 × 9.5 =	24.9 Calories per °C
CH ₄	0.14 × 8.8 =	1.2 Calories per °C
H ₂	0.28 × 6.98 =	2.0 Calories per °C
CO, N ₂	17.74 × 7.01 =	124.4 Calories per °C

$$\text{Total} = \dots \quad 152.5 \text{ Calories per } ^\circ\text{C}$$

$$\text{Total heat content} = 152.5(173 - 18) = \dots \quad 23,650 \text{ Calories}$$

10. Heat content of water vapor in gas.

$$\text{Mols of H}_2\text{O in gas} = \dots \quad 0.66 \text{ kg-mol}$$

$$\text{Molal humidity} = 0.66/20.78 = \dots \quad 0.0318$$

$$\text{Dew-point (Fig. 10)} = \dots \quad 76^\circ \text{ F}(24^\circ \text{ C})$$

$$\text{Heat of vaporization at } 76^\circ \text{ F} = 18,880/1.8 = \dots \quad 10,490 \text{ Calories per kg-mol}$$

$$\text{Total heat content of water vapor} =$$

$$0.66[10,490 - 18(24 - 18) + 8.4(173 - 18)] = \dots \quad 7,850 \text{ Calories}$$

11. Heat content of slag. S. Umino¹ determined the relative heat content of various blast-furnace and open-hearth-furnace slags and has found that the heat contents of these two types of slags are nearly the same when measured at the same temperature. These values are shown graphically in Fig. 63. It will be seen that there is no sudden break in the heat content-temperature curve, thus indicating that no sudden transformations take place in cooling and that the slag exists essentially in the form of a glass. From Fig. 63 it will be seen that at a temperature of 1360° C the heat content of slag is 365 Calories per kg.

$$\text{Total heat content of slag} = 365 \times 63.8 = \dots \quad 23,290 \text{ Calories}$$

12. Heat content of pig iron. The average heat content of molten pig iron from blast furnaces has also been determined by S. Umino.² Although the composition of the pig iron used in his experiments is not identical with the one under discussion, nevertheless the compositions are sufficiently alike to justify use of the same values of heat content. At a pouring temperature of 1360° C this heat content corresponds to a value of 300 Calories per kg. This value includes the sensible heat contents of the solid and liquid states, the latent heat of fusion, and the heat evolved in the separation and decomposition of cementite, Fe₃C, from solution in the iron.

$$\text{Total heat content of pig iron} = 100 \times 300 = \dots \quad 30,000 \text{ Calories}$$

$$\text{13. Heat absorbed by cooling-water} = 576 \times 13 = \dots \quad 7,490 \text{ Calories}$$

¹ S. Umino, Science Reports, Tokoku Imperial University, 17, 985 (1928).² Idem, 16, 575 (1927).

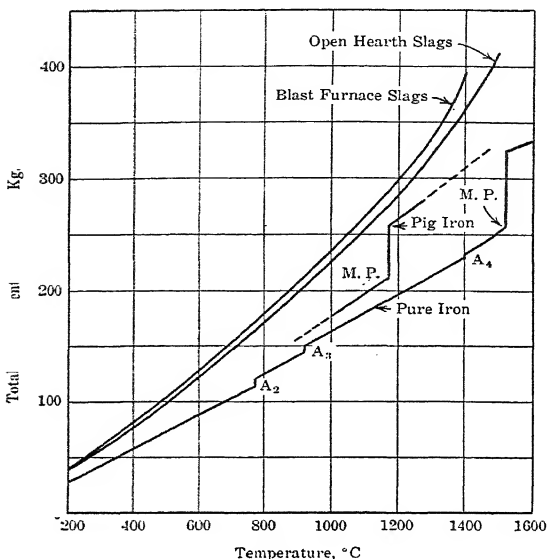


Fig. 63. Total Heat Contents of Irons and Slags, referred to 18° C.

Data taken from

S. Umino, Tokohu Imperial University 17, 985 (1928) for slags.
 S. Umino, " " " 16, 575 (1927) for pig iron.
 S. Umino, " " " 18, 91 (1929) for pure iron.

Composition of Slags

	Blast Furnace Slags			Open-Hearth Slags		
	2	3		4	5	6
SiO ₂	34.50	37.26	34.22	18.20	18.28	20.28
FeO.....	1.58	0.82	0.74	13.45	10.27	10.47
Fe ₂ O ₃	0.29	0.84	0.20	2.40	3.63	2.50
CaO.....	40.92	43.15	41.80	42.63	43.55	44.20
MgO.....	3.90	1.80	4.56	9.14	11.84	10.47
P.....	trace	trace	trace	0.33	0.25	0.25
S.....	0.98	0.11	0.90	0.54	0.45	0.40
MnO.....	2.24	1.82	1.88	6.97	6.60	6.60
Al ₂ O ₃	15.48	13.15	15.60	5.00	4.68	4.79
Apparent Sp. Gr. 20° C.....	2.80	2.94	2.97	3.46	3.56	3.12

Composition of Pig Iron

C = 4.31%
 Si = 1.11%
 Mn = 0.53%
 P = 0.12%
 S = 0.022%
 Cu = 0.21%

Thermal Data on Pure Iron

Heat of transition A₂ (α to β) 6.5 Calories per kg
 Heat of transition A₃ (β to γ) 5.6 Calories per kg
 Heat of transition A₄ (γ to δ) 1.9 Calories per kg
 Heat of fusion 65.6 Calories per kg

Heat of Fusion = 46.63 Calories per kg

Summary of Heat Balance.

<i>Input</i>		
Heat of partial combustion of charcoal.....	341,900 Calories	91.6%
Heat content of air.....	31,200 Calories	8.4%
Total.....	373,100 Calories	100.0%
<i>Output</i>		
Heat absorbed in reduction of iron oxides...	153,800 Calories	41.3%
Heat absorbed in reduction of Mn_2O_4	6,240 Calories	1.7%
Heat absorbed in reduction of SiO_2	10,850 Calories	2.9%
Heat absorbed in calcination of carbonates .	15,770 Calories	4.2%
Heat content of dry gas.....	23,650 Calories	6.4%
Heat content of water vapor.....	7,850 Calories	2.1%
Heat content of slag.....	23,290 Calories	6.1%
Heat content of pig iron.....	30,000 Calories	8.1%
Heat absorbed by cooling-water.....	7,490 Calories	2.0%
Heat losses unaccounted for (by difference).	94,160 Calories	25.2%
Total.....	373,100 Calories	100.0%

This balance is summarized in Fig. 64, page 324.

PROBLEMS

1. In a plant for the manufacture of sulphuric acid by the chamber process pyrites are burned in a shelf burner. The gases from the burner enter the Glover tower at 480°C and leave this tower at 105°C , entering the first chamber. The gases leave the last chamber at 42°C and finally leave the Gay-Lussac tower at 21°C . On the basis of 100 kg of pyrites, as charged, there are charged into the Glover tower, 175 kg of chamber acid, 65.2% H_2SO_4 (51.8° B \acute{e}) at 30°C ; 610 kg of Gay-Lussac acid at 23°C , and 1.30 kg of 40% nitric acid at 20°C . The Gay-Lussac acid contains 78.0% H_2SO_4 (60.0° B \acute{e}), 0.984% N_2O_3 in solution, and 21.0% H_2O .

The analyses of the pyrites, cinders, and the moisture-free gases leaving the burner are as follows:

<i>Pyrites</i>	<i>Cinder</i>	<i>Gases (by volume)</i>
FeS ₂ 90.00%	Fe ₂ O ₃ 89.80%	O ₂ 9.32%
SiO ₂ 4.80%	FeS ₂ 1.65%	N ₂ 82.38%
H ₂ O 5.20%	SO ₂ 1.93%	SO ₂ 8.00%
	SiO ₂ 6.62%	SO ₃ 0.30%
100.00%	100.00%	100.00%

The pyrites is charged to the burner at 20°C . The air enters at 20°C , under a barometric pressure of 722 mm of Hg and with a percentage humidity of 40%. The cinders are withdrawn at 320°C .

For each 100 kg of pyrites as charged, 768 kg of acid containing 79.4% H_2SO_4 leave the Glover tower at 100°C and are cooled to 23°C . The chamber acid leaves the first chamber at 65°C and is cooled to 30°C before entering the Glover tower.

The acid leaves the Gay-Lussac tower at 30°C and is cooled to 23°C for recirculation. The spray water enters the chambers at 20°C .

From the flow-chart and assumptions of Illustration 1, calculate individual weight and heat balances, on the basis of 100 kg of pyrites as fired, of:

- The burner.
- The Glover tower
- The chambers.
- The Gay-Lussac tower.
- The entire plant.

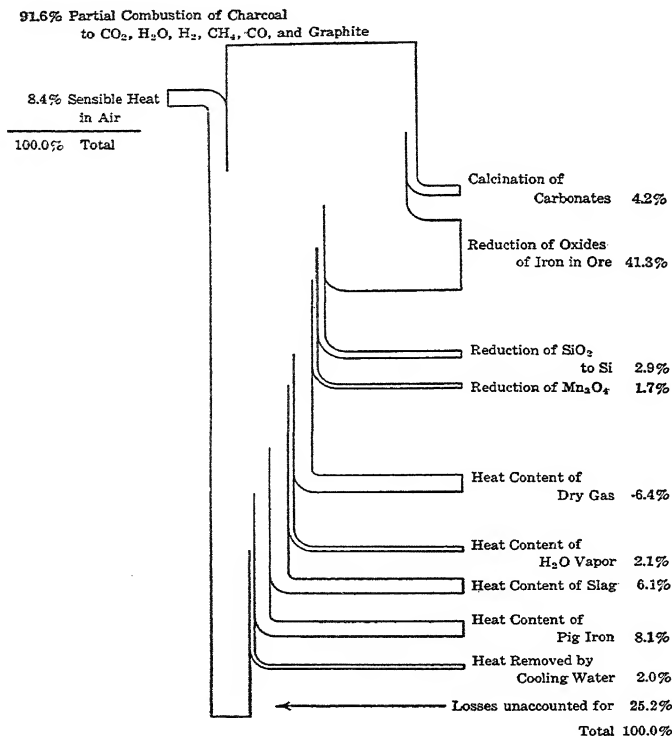


FIG. 64. Heat Balance of a Blast Furnace.

2. The charge delivered to a blast furnace, on the basis of 1000 lb of pig iron, consists of 1810 lb of ore, 361 lb of limestone, and 892 lb of coke. The analyses of various components of the charge are as follows:

<i>Ore (1810 lb)</i>		<i>Limestone (361 lb)</i>		<i>Coke (892 lb)</i>	
Fe ₂ O ₃	62.10%	CaO	51.12%	Carbon	88.20%
FeO	19.07%	MgO	2.10%	Hydrogen	2.00%
Mn ₂ O ₄	2.12%	SiO ₂	2.89%	Fe ₂ O ₃	2.10%
Al ₂ O ₃	2.89%	Al ₂ O ₃	4.12%	SiO ₂	1.98%
SiO ₂	8.62%	Fe ₂ O ₃	0.52%	CaO	2.32%
H ₂ O	5.20%	CO ₂	35.05%	MgO	1.10%
	<hr/>	H ₂ O	4.20%	S	0.20%
	100.00%		<hr/>	H ₂ O	2.10%
			100.00%		<hr/>
					100.00%

The total heating value of the coke is 14,200 Btu per lb.

On the basis of 1000 lb of pig iron produced, 51 lb of dust are collected from the gases leaving the furnace. The analyses of the products are as follows:

<i>Pig iron (1000 lb)</i>		<i>Flue dust (51 lb)</i>		<i>Gas analysis (by volume)</i>	
Fe	92.28%	FeO	83.2%	CH ₄	0.80%
Si	2.10%	C	10.1%	CO ₂	12.10%
Mn	1.38%	CaO	3.1%	CO	29.30%
S	0.03%	SiO ₂	3.6%	H ₂	2.12%
C	4.21%		<hr/>	O ₂	0.20%
	<hr/>		100.0%	N ₂	55.48%
	100.00%				<hr/>
					100.00%

The surrounding air is at 70° F, 40% percentage humidity and a barometric pressure of 29.2 in. of Hg. This air is heated and supplied to the tuyères at 850° F.

The ore, flux, and coke are charged at an average temperature of 65° F.

The gases leave the furnace at a temperature of 422° F. The molten slag and pig iron are tapped from the furnace at a temperature of 2500° F. The sensible heat content of the flue dust is negligible.

Calculate the complete weight and heat balances of this furnace, using the assumptions of Illustration 2.

PART II

CHAPTER X

CALCULATIONS OF CRYSTALLIZATION, ADSORPTION, AND DISTRIBUTION

The dissolution of a liquid or solid substance by a liquid is in many respects analogous to the vaporization of a liquid into a gas. In the crystalline state of aggregation the constituent atoms are held together in a rigid structure by strong mutual attractive forces. Opposed to these are other forces resulting from the inherent kinetic energy of translation which is possessed by each particle of matter in a quantity dependent upon its temperature. At the surface of a solid some of the particles become sufficiently energized to break away from the attractive forces which hold them in the solid state and disperse themselves into the vapor state. As previously pointed out, solid substances exert definite equilibrium vapor pressures. In general the vapor pressures of solids are small and the concentrations of the solid particles which are in the dispersed or vapor state are correspondingly low.

LIQUID SOLUTIONS

A substance which is a solvent for a solid has an entirely specific effect upon the distribution of particles between the solid and its dispersed state. Thus a substance which may be an excellent solvent for one solid may exert no appreciable influence on another. The solvent action of a liquid is presumed to result from a high affinity or attractive force between the liquid and the solid particles. When a solvent and a solid are brought into contact with each other, the attractive forces of the liquid aided by the thermic motion of the solid particles tend to break apart the structure of the solid and to disperse molecules from its surface. As a result, ions or molecules are enabled to break away from the forces holding them to the solid and to enter the liquid as individually mobile units, thus forming what is termed a *solution* of the solid in the liquid. The dispersed material in a solution is termed the *solute*. This distinction between the solvent and solute in a solution is entirely arbitrary since either component may be considered as either solute or solvent. For example, a solution of naphthalene in benzene may equally well be considered as a solution of benzene in naphthalene.

The solute particles of a solution are free to move about as a result of the kinetic energy of translation which is possessed by each. By hom-

barding the confining walls these particles exert an *osmotic pressure* which is entirely analogous to the partial pressure exerted by each component of a gaseous mixture. Thus, when a solution is in contact with the solid from which it was formed, there will be a continual return of dissolved particles to the solid surface. The dispersion of a solid into a liquid is termed *dissolution*. The reverse process is known as *crystallization*. As dissolution proceeds, the concentration of dispersed particles is increased, resulting in an increased osmotic pressure and a greater rate of crystallization. When the solute concentration becomes sufficiently high, the rate of crystallization will equal the rate of dissolution, and a dynamic equilibrium will be established, the concentration of the solution then remaining constant. This equilibrium is analogous to that between a liquid and its vapor. Under these conditions the solution is said to be *saturated* with the solute and is incapable of dissolving greater quantities of that particular solute.

The concentration of solute in a saturated solution is termed the *solubility* of the solute in the solvent. Solubilities are dependent on the nature of the solute, the nature of the solvent, and the existing temperature. The effect of pressure on solubility may be neglected ordinarily. However, in a solution whose volume is less than the sum of the volumes of its components in their pure states, solubility is increased by an increase in pressure. In the opposite case in which the total volume is increased in the formation of a solution, an increase in pressure lowers the solubility.

The simple generalizations which apply to equilibria between liquids and vapor-gas mixtures are not applicable to liquid solutions. Little is known regarding the relationships between solubilities and the specific properties of the solute and solvent. The properties of each particular system must be individually determined by experimental means, and it is impossible to predict quantitatively the behavior of one system from that of another. This results from the fact that what may be termed the *solution pressure* of a solid is entirely dependent on the nature of the solvent with which it is in contact. In many cases it is impossible to predict, even qualitatively, the effect of temperature on solubility.

Compositions of Solutions. Six methods for the expression of the composition of a solution are in general use:

1. Percentage of solute by weight.
2. Weight of solute per unit weight of solvent.
3. Mols of solute per unit weight of solvent.
4. Mol fraction of solute.
5. Mols or equivalent weights of solute per unit volume of solution.
6. Weight of solute per unit volume of solution.

The first three methods of expression are most satisfactory for industrial calculations wherein solutions are involved. The second and third methods possess the merit of expressing concentration on the basis of a constant quantity of solvent. Considerable simplification results from the use of these methods in problems involving crystallization. Where the thermal and stoichiometric changes which accompany dissolution and crystallization are to be considered, the third method possesses the significant advantage of expressing concentrations in terms of molal quantities. For this reason, concentrations in the following sections will be expressed in terms of mols of solute per 1000 units of weight of solvent. The concentration of a solution when expressed in this unit is termed its *molality*. The molality of a solution numerically represents the number of pound-mols of solute per 1000 pounds of solvent, or the number of gram-mols of solute per 1000 grams of solvent.

The mol fraction of a solute in a solution is the ratio of the number of mols of solute to the sum of the total number of mols of solute and solvent. This method of expression is convenient in plotting the constitutional diagrams of solutions showing solubilities and phase relations in terms of temperature and composition.

The fifth and sixth methods of expression are most convenient in volumetric analysis because of the ease of measuring liquid volumes. Solutions are ordinarily measured volumetrically and expressed in volume units for both industrial and analytical purposes. For this purpose, method 6 is very widely used. Common units are grams of solute per 100 cubic centimeters of solution and pounds of solute per gallon of solution. Such methods, in which the concentration is expressed on a volumetric basis, have the disadvantage of being dependent on the temperature of the solution. When expressed in these terms, the concentration of the solute in a given solution is a function of the density of the solution and therefore of the temperature. Hence a complete expression of concentration on a volumetric basis must include a specification of the temperature. However, in many cases the change of volume of a solution is negligible over a wide temperature range. For example, water in being heated from 4° to 50° C undergoes a change in density of only 1 per cent. However, many solutions, especially in organic solvents, exhibit much more rapid changes in density with temperature. Aqueous solutions of salts also may show considerably higher temperature coefficients of expansion than does water alone.

Concentrations of solutions may be readily converted from one mode of expression to another by methods similar to those used in the case of gaseous mixtures. Where it is desired to convert from a volumetric method, such as method 5 or 6, to a method based on unit weight,

it is necessary that data be available regarding the density of the solution.

Illustration 1. A solution of sodium chloride in water is found to contain 23 grams of NaCl per 100 cc of solution at 20° C. The density of the solution at this temperature is 1.148 grams per cubic centimeter.

Calculate the concentration of the solution as expressed by each of the methods described above.

Basis: 100 cc of solution weighing, 114.8 grams.

NaCl = 23 grams or $23/58.5 = \dots\dots\dots$	0.393 gram-mol
Water = $114.8 - 23 = 91.8$ grams or $\dots\dots\dots$	5.1 gram-mols

1. Percentage NaCl by weight = $23/114.8 = 20.0$.
2. Grams NaCl per gram of water = $23/91.8 = 0.251$ or 25.1 grams per 100 grams of water.
3. Gram-mols of NaCl per 1000 grams of water, $0.393 \times 1000/91.9 = 4.28 = \text{molality}$.
4. Mol fraction of NaCl = $0.393/(0.393 + 5.1) = 0.0715$.
5. Gram-mols of NaCl per 100 cc of solution = $23/58.5 = 0.393$.

Densities and Specific Gravities of Liquids. *Densities* of liquids are expressed either in grams per cubic centimeter or in pounds per cubic foot. The density of water at 4° C is 1.0000 gram per cubic centimeter or 62.43 pounds per cubic foot.

The *specific gravity* of a liquid is the ratio of its density to the density of water at some specified reference temperature. The temperatures corresponding to a value of specific gravity are generally symbolized by a fraction, the numerator of which is the temperature of the liquid in question, and the denominator the temperature of the water which serves as the reference. Thus the term sp. gr. 70/60° F indicates the specific gravity of a liquid at 70° F referred to water at 60° F, or the ratio of the density of the liquid at 70° F to that of water at 60° F. It is apparent that if specific gravities are referred to water at 4° C (39.2° F) they will be numerically equal to densities in grams per cubic centimeter.

The densities of solutions are functions of both concentration and temperature. The relationships between these three properties have been determined for a majority of the common systems. Such compilations as the International Critical Tables contain extensive tabulations giving the densities of solutions of varying concentrations at specified temperatures. These data are most conveniently used in graphical form in which density is plotted against concentration. Each curve on such a chart will correspond to a specified, constant temperature. The density of a solution of any concentration at any temperature may be readily estimated by interpolation between these curves. In Fig. 65 are plotted the densities of solutions of sodium chloride at various tem-

peratures. It is convenient to use two methods of expression of concentration in preparing such charts, one on a volumetric and the other on a weight basis.

For a given system of solute and solvent the density or specific gravity at a specified temperature may serve as an index to the concentration. This method is useful only when there is a large difference between the densities of the solutions and the pure solvent. In several industries specific gravities have become the universally accepted means of indicating concentrations, and products are purchased and sold on the basis of

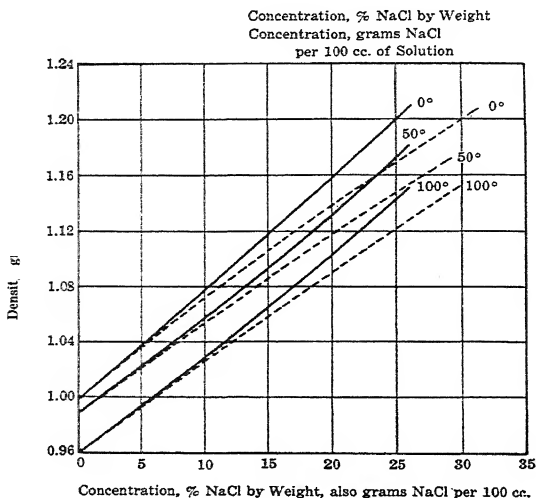


Fig. 65. Densities of Aqueous Sodium Chloride Solutions.

specific gravity specifications. Sulphuric acid, for example, is marketed almost entirely on this basis. Specific gravities are also made the basis for the control of many industrial processes in which solutions are involved. To meet the needs of such industries, special means of numerically designating specific gravities have been developed. Several scales are in use in which specific gravities are expressed in terms of *degrees* which are related to specific gravities and densities by more or less complicated and arbitrarily defined functions.

Baumé Gravity Scale. Two so-called Baumé gravity scales are in common use, one for use with liquids lighter and the other for liquids

heavier than water. The former is defined by the following expression:

$$\text{Degrees Baumé} = \frac{140}{S} - 130$$

where S is the specific gravity at 60/60° F. It is apparent from this definition that a liquid having the density of water at 60° F (0.99904 gram per cubic centimeter) will have a gravity of 10° Baumé. Lighter liquids will have *higher* gravities on the Baumé scale. Thus, a material having a specific gravity of 0.60 will have a gravity of 103° Baumé.

The Baumé scale for liquids heavier than water is defined as follows:

$$\text{Degrees Baumé} = 145 - \frac{145}{S}$$

Gravities expressed on this scale increase with increasing density. Thus, a specific gravity of 1.0 at 60/60° F corresponds to 0.0° Baumé, and a specific gravity of 1.80 corresponds to 64.44° Baumé. It will be noted that both the Baumé scales compare the densities of liquids at 60° F. In order to determine the Baumé gravity, the specific gravity at 60/60° F must either be directly measured or estimated from specific-gravity measurements at other conditions. The Baumé gravity of a liquid is thus independent of its temperature. Readings of Baumé hydrometers at temperatures other than 60° F must be corrected for temperature so as to give the value at 60° F.

A. P. I. Scale. As a result of confusion of standards by instrument manufacturers, a special gravity scale has been adopted by the American Petroleum Institute for expression of the gravities of petroleum products. This scale is similar to the Baumé scale for liquids lighter than water as indicated by the following definition:

$$\text{Degrees A. P. I.} = \frac{141.5}{S} - 131.5$$

As on the Baumé scale, a liquid having a specific gravity of 1.0 at 60/60° F has a gravity of 10°. However, a liquid having a specific gravity of 0.60 has an A. P. I. gravity of 104.3 as compared to a Baumé gravity of 103.3. The gravity of a liquid in degrees A. P. I. is determined by its density at 60° F and is independent of temperature. Readings of A. P. I. hydrometers at temperatures other than 60° F must be corrected for temperature so as to give the value at 60° F.

A. P. I. gravities are readily converted by Fig. 96, p. 475.

Twaddell Scale. The Twaddell scale is used only for liquids heavier than water. Its definition is as follows:

$$\text{Degrees Twaddell} = 200(S - 1.0)$$

This scale has the advantage of a very simple relationship to specific gravities.

Numerous other scales have been adopted for special industrial uses, for example, the Brix scale for measuring directly the concentration of sugar solutions.

Solubilities of Solids Which Do Not Form Compounds with the Solvent. In general, where no true chemical compounds are formed be-

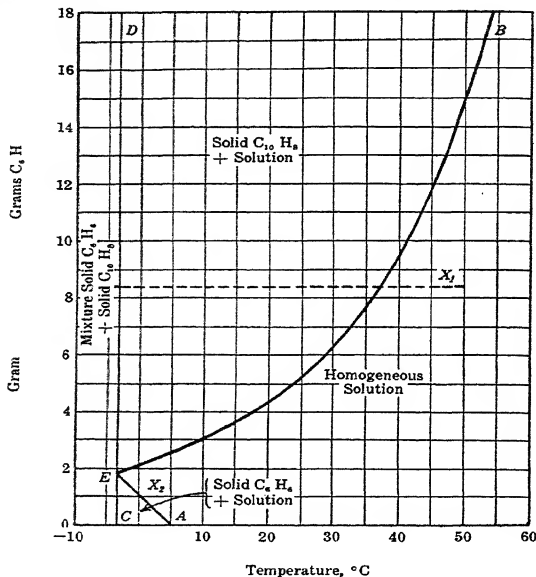


FIG. 66. Solubility of Naphthalene in Benzene.

(Eutectic forms at $-3.5^{\circ}\text{C}.$; 1.83 gram-mols per 1000 grams benzene.)

tween a solute and solvent, the solubility increases with increasing temperature. The solubility curves of such systems resemble vapor-pressure curves in general form. In Fig. 66 are plotted the solubility data of a typical system, naphthalene in benzene. Similar curves express the solubility data of a variety of other solutes both organic and inorganic in both aqueous and non-aqueous solutions.

Curve *EB* of Fig. 66 represents the conditions of temperature and concentration which correspond to saturation with *naphthalene* of a solution of naphthalene in benzene. A solution whose concentration

and temperature fix a point on this curve will remain in dynamic equilibrium with solid crystals of naphthalene. If the temperature is lowered or the concentration increased by the removal of solvent, naphthalene crystals will be formed in the solution. The area to the right of curve *EB* represents conditions of homogeneous, partially saturated solutions. The area between curves *EB* and *ED* represents conditions of non-homogeneous mixtures of crystals of pure naphthalene in solutions of naphthalene in benzene. If a solution whose concentration and temperature are represented by point x_1 is cooled without change in composition, its conditions will vary along the dotted line parallel to the temperature axis. The temperature at which this dotted line intersects the solubility curve *EB* is the temperature at which pure naphthalene will begin to crystallize from the solution. As the temperature is reduced further, more naphthalene will crystallize and the remaining saturated solution will diminish in concentration, its condition always represented by a point on curve *EB*. When the temperature corresponding to line *CED* is reached the system will consist of pure naphthalene crystals and a saturated solution whose concentration corresponds to point *E*. Further decrease in temperature will cause this remaining solution to solidify to a mixture of crystals of pure benzene and pure naphthalene. The line *CED* represents the completion of solidification, and the area to the left of it corresponds to completely solid systems of naphthalene and benzene crystals.

The point *E* is termed the *eutectic point*, and the corresponding temperature and composition are, respectively, the *eutectic temperature* and the *eutectic composition*. If a solution of eutectic composition is cooled it will undergo no change until reaching the eutectic temperature, when it will completely solidify without further change in temperature. A solution of eutectic composition solidifies completely at one definite temperature which is also the lowest solidification point possible for the system.

The curve *EA* represents the conditions of temperature and composition which correspond to saturation with benzene of a solution of naphthalene in benzene. Whereas curve *EB* represents the solubility of naphthalene in benzene, curve *EA* represents the solubility of benzene in naphthalene. The area *AEC* represents conditions of non-homogeneous mixtures of benzene crystals in saturated solutions of naphthalene in benzene. If a solution whose composition and temperature are represented by point x_2 is cooled, its conditions will vary along the horizontal dotted line. At the temperature of the intersection of this line with curve *EA*, crystals of pure benzene will be formed. As the temperature is further reduced, more pure benzene will crystallize, and the

remaining saturated solution will vary in composition along curve EA towards E . When the eutectic temperature is reached, the remaining saturated solution will be of eutectic composition, represented by point E . Further decrease in temperature will cause complete solidification into a mixture of benzene and naphthalene crystals.

The curve EA is frequently termed the *freezing-point curve* of the solution representing the temperatures at which solvent begins to freeze out. The point A represents the freezing-point of the pure solvent, benzene. From the same viewpoint the curve EB might be considered as a freezing-point curve along which solute begins to freeze out. Thus, either curve may be considered as a solubility curve or a freezing-point curve.

The *percentage saturation* of a solution may be defined as the percentage ratio of the existing weight of solute per unit weight of solvent to the weight of solute which would exist per unit weight of solvent if the solution were saturated at the existing temperature. The percentage saturation of a solution may be varied by changing either its temperature or composition. The effects of such changes on the percentage saturation of a solution may be predicted by locating the point representing the conditions of the solution on a solubility chart such as Fig. 66. A change in temperature will move this point along a line parallel to the temperature axis. A change in composition will move it along a line parallel to the concentration axis. A process in which both composition and temperature are changed simultaneously is best considered as proceeding in two steps: a change in composition at constant temperature and a change in temperature with constant composition.

Solubilities of Solids Which Form Solvates with Congruent Points. Many solutes possess the property of forming definite chemical compounds with their solvents. Such compounds of definite proportions between solutes and solvents are termed *solvates*, or if the solvent is water, *hydrates*. Several solvates of different compositions may be formed by a single system, each a stable form, under certain conditions of temperature and composition. The presence of such solvates greatly complicates the solubility relationships of the system.

The system ferric chloride and water is an excellent illustration of the effects of the formation of many hydrates. In Fig. 67 are plotted the solubility curves of this system. Point A represents the freezing-point of the pure solvent, water, and line AB the conditions of equilibrium in a solution which is saturated with the solid solvent, ice. This curve is analogous to curve AE of Fig. 66 and represents the solubility of water in ferric chloride. The area ABI represents non-homogeneous mixtures of pure ice in equilibrium with saturated solutions.

Point *B* of Fig. 67 is a eutectic point analogous to point *E* of Fig. 66. Line *BC* represents the conditions of saturation of a solution of ferric chloride in water with the solid hydrate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. If a solution, whose conditions are represented by point x_1 , is cooled, it will become saturated with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ when conditions corresponding to this

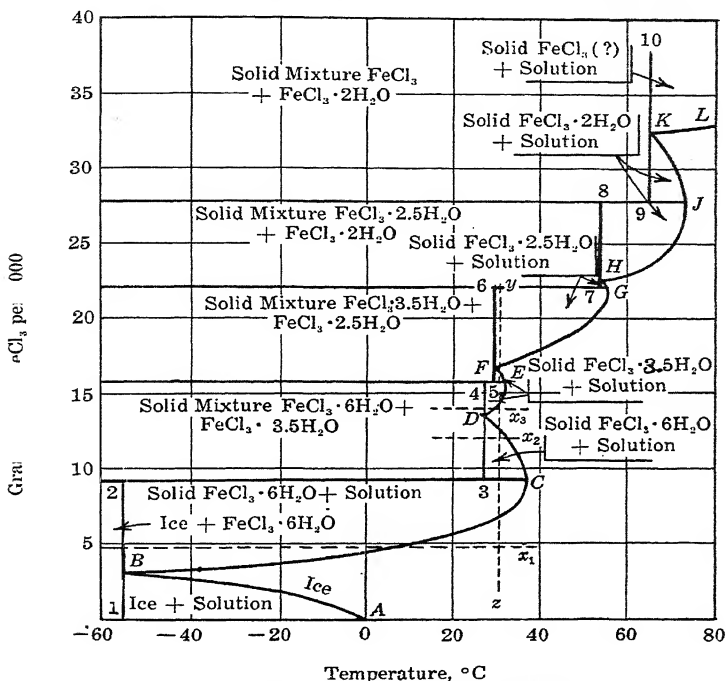


FIG. 67. Solubility of Ferric Chloride in Water.

concentration on curve *BC* are reached. Further cooling will result in separation of crystals of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ which will be in equilibrium with saturated solutions whose compositions correspond to the ordinates of curve *BC* at the existing temperatures. If cooling is continued, more $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ crystals will be formed and the concentration of the remaining solution diminished along curve *BC* until it reaches a value of *B*, corresponding to the eutectic temperature. On further cooling the remaining solution will solidify, without change in temperature, into a

mixture of crystals of pure ice and pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The area $BC\mathcal{Q}$ represents non-homogeneous mixtures of pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ crystals and saturated solutions. The area to the left of curve $1B\mathcal{Q}$ represents mixtures of crystals of pure ice and pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, which are not soluble in each other in the solid state.

As the concentration and temperature of a saturated solution are increased along curve BC , a concentration corresponding to point C is reached, which is the composition of the pure hydrate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. At this point the entire system must be solid hydrate in equilibrium with solution of the same composition. If a solution of this composition is cooled, when its temperature reaches that of point C it will completely solidify into $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ without change of temperature. This behavior is entirely analogous to the freezing of a pure compound, and the temperature of point C represents the melting-point of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. A point such as C , at which a hydrate is in equilibrium with saturated solution of the same composition, is termed a *congruent point*. The curves $ABC\mathcal{Q}1$ may be considered as representing the complete solubility-freezing-point relationship of a system in which water is the solvent and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ the solute. Point A is the melting-point of the pure solvent and C that of the pure solute; B represents the eutectic point of this system.

From the negative slope of curve CD it follows that, at concentrations higher than that of point C , the concentration of FeCl_3 in a saturated aqueous solution may be increased by *lowering* the temperature. This behavior may be readily understood by considering that the curves $\mathcal{Q}CDE4$ represent the solubility-freezing-point data of an entirely new system in which the solvent is $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and the solute is $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$. On this basis curve CD is entirely analogous to AB and represents the conditions of equilibrium between pure, solid solvent, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and a solution of $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$ in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. If a solution at conditions represented by point \mathcal{Q}_2 is cooled, pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ will crystallize out when a temperature corresponding to this concentration on curve CD is reached. Further cooling will result in the formation of more pure solvent crystals, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and the remaining saturated solution will increase in concentration, along curve CD . When the temperature of curve $4D\mathcal{S}$ is reached this remaining solution will have the composition of point D . Further cooling will result in complete solidification, without further change in temperature, into a mixture of crystals of pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and pure $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$. Point D represents the eutectic point of this system and is entirely analogous to point B . The area $CD\mathcal{S}$ represents conditions of non-homogeneous mixtures of pure crystals of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and saturated solutions of $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$ in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Curve DE represents the conditions of equilibrium between crystals of pure solute, $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$, and a saturated solution of $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$ in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. As the concentration and temperature of a saturated solution are increased along curve DE , a concentration corresponding to point E is reached which is the composition of the hydrate $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$. At this point the entire system must be solid $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$ in equilibrium with solution of the same concentration. Point E is, therefore, a second congruent point, representing the melting-point of $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$. Area $DE4$ represents conditions of non-homogeneous mixtures of crystals of pure $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$ and saturated solutions. The area to the left of curve $SD4$ represents entirely solid systems composed of mixtures of crystals of pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$.

By exactly similar reasoning, the curves $5EFG6$ may be considered as representing the solubility-freezing-point data of a system in which the solute is $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$ and the solvent $\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$. Curves $7GHJ8$ represent the system of $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, solute, and $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$, solvent. Curves $9JKL$ represent the system of FeCl_3 , solute, and $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, solvent. Points F , H , and K are the eutectic points of these systems. Points G and J are the congruent melting-points of $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, respectively. —

By means of a chart such as Fig. 67 the changes taking place in even very complicated systems may be readily predicted or explained. An illustration of the peculiar phenomena which may take place in complex systems is furnished by the isothermal concentration of a dilute aqueous solution of ferric chloride along the line zy . Such concentration may be carried out by evaporation at constant temperature. At the intersection of zy with BC , crystals of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ will begin to form. At line $C2$ the system will be entirely solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Further concentration results in the appearance of liquid solution, and at curve CD the system will be once more entirely liquid. As concentration is continued to curve DE , solidification again begins, becoming complete at line $E5$. Further concentration causes the reappearance of liquid, and liquefaction is completed at curve EF . At curve FG solidification begins and becomes complete at $G6$. This surprising alternation of the liquid and solid states while concentration is progressing may be easily demonstrated.

Many other systems, both organic and inorganic, behave in a manner similar to that of aqueous ferric chloride and form one or more solvates and congruent points.

Solubilities of Solids Which Form Solvates without Congruent Points. In certain systems solvates are formed which are not stable and which decompose before the temperature of a congruent point is reached. Such solvates undergo direct transition from the solid state into other

chemical compounds. These transitions take place at sharply defined temperatures which are termed *transition points*. The system of sodium sulphate and water illustrates this type of behavior. In Fig. 68 are plotted the solubility and freezing-point data of this system.

Curve *AB* of Fig. 68 represents conditions of equilibrium between ice and aqueous solutions of sodium sulphate. Point *B* is the eutectic point of the system of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (solute) and water (solvent). Curve

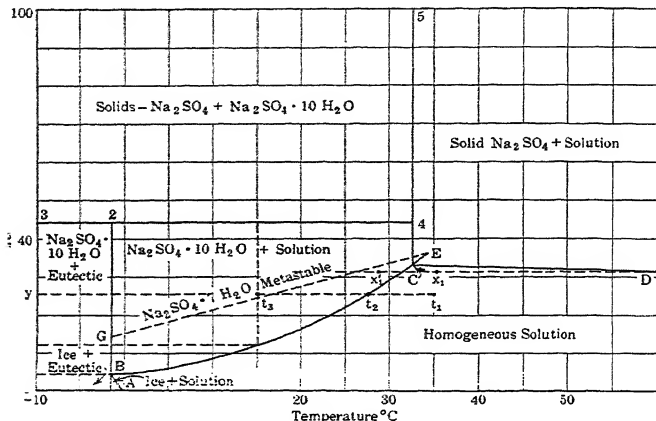


FIG. 68. Solubility of Sodium Sulphate in Water.

BC represents the equilibrium between crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and saturated solution. As the temperature of the system is increased the concentration of the saturated solution increases along curve *BC*. Normally this increase would continue until a congruent point was reached. However, at a temperature of 32.384°C , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ becomes unstable and is decomposed into Na_2SO_4 and water. The solubility of the anhydrous Na_2SO_4 as indicated by curve *CD* diminishes with increasing temperature. Points on this curve represent conditions of equilibrium between crystals of anhydrous Na_2SO_4 and saturated solutions. A solution whose conditions are represented by point x_1 will become saturated if either heated or cooled sufficiently. If cooled, crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ will form when the conditions of curve *BC* are reached. If heated, crystals of anhydrous Na_2SO_4 will form at the temperature corresponding to composition x_1 on curve *CD*.

The significance of the areas of Fig. 68 is similar to that of the other diagrams which have been discussed. The area of the small triangle to

the left of line AB represents a region of equilibrium between crystals of pure ice and saturated solution. Area $BC42$ is a region of equilibrium between crystals of pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and saturated solution. The area to the left of line $B2$ represents a solid mixture of crystals of ice and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Line $C45$ indicates the transition temperature at which the decahydrate decomposes to form the anhydrous salt. Line 324 indicates the composition of the pure decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The area to the right of curve $54CD$ represents conditions of equilibria between crystals of pure Na_2SO_4 and saturated solutions. The area above and to the left of curves 3245 is a region of entirely solid mixtures of Na_2SO_4 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Line 45 therefore represents a temperature of complete solidification.

Many systems which form several solvates show solubility relationships both with and without congruent points and transition points in the same system. For example, zinc chloride forms five hydrates. Four of these hydrates decompose, as does $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, exhibiting transition points before congruent concentrations are reached. The fifth hydrate, $\text{ZnCl}_2 \cdot 2.5\text{H}_2\text{O}$, exhibits a true congruent point as do the hydrates of ferric chloride. The significance of such solubility relationships may be understood from the principles discussed in the preceding sections.

Effect of Particle Size on Solubility. The solution pressure and solubility of a solid is affected by its particle size in a manner entirely analogous to the effect of particle size on vapor pressure. The solubility of a substance is increased with increase in its degree of subdivision. This increasing solubility with diminishing particle size is demonstrated by the behavior of crystals which are in equilibrium with their saturated solutions. Where such an equilibrium exists the total amounts of solid and liquid must remain unchanged. However, the equilibrium is dynamic, resulting from equality between the rates of dissolution and crystallization. As a result of the effect of particle size on solubility, the small crystals in such a solution will possess higher solution pressures than the large ones and will tend to disappear with corresponding increase in size of the large crystals. This growth of large crystals at the expense of the small ones in a saturated solution is a familiar phenomenon of considerable industrial importance. For the same reasons, an irregular crystalline mass will change its shape in a saturated solution. The sharp corners and points will exert higher solution pressures than the plane surfaces and will disappear, building up the plane surfaces and tending to produce a regular shape. Like vapor pressures, solubilities are not noticeably affected by particle size until submicroscopic dimensions are approached.

Supersaturation. Just as spontaneous condensation of a vapor is made difficult because of the high vapor pressure of small drops, spontaneous crystallization is interfered with by the high solubility of small crystals. In order to produce spontaneous crystallization the concentration of a solution must be sufficiently high that the small crystalline nuclei which are formed by simultaneous molecular or ionic impacts do not immediately redissolve. Such a concentration will be much greater than that which is in equilibrium with large crystals of the same solid. Once crystallization is started and nuclei are formed it will continue and the nuclei will grow until the normal equilibrium conditions are reached. For these reasons it is relatively easy to obtain solutions whose concentrations are higher than the values normally corresponding to saturation. Such solutions are *supersaturated* with respect to large crystals but are only partially saturated with respect to the tiny nuclei which tend to form in them. Supersaturated solutions may be formed by careful exclusion of all crystalline particles of solute and by slow changes in temperature or concentration without agitation.

Because of the phenomenon of supersaturation, it is possible to extend the curves of solubility diagrams, such as Fig. 68, into regions where the equilibria which they represent would not normally be stable. The dotted curves of Fig. 68 represent such equilibria which have been experimentally observed in supersaturated solutions of this system. Such equilibria are termed *metastable* and possess the continual tendency to revert to the normal, stable state corresponding to their conditions of temperature and concentration.

The dotted curve *GE* of Fig. 68 represents the metastable equilibrium between crystals of $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and its saturated solutions. If a solution of conditions x_1 is carefully cooled, normal crystallization of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ may be prevented and a supersaturated solution produced at conditions x_1' . If cooling is continued the crystallization of $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ may be induced at a temperature corresponding to composition x_1 on curve *GE*. A supersaturated solution at conditions x_1' is capable of dissolving $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and is unsaturated with respect to this compound. On the other hand, its conditions are unstable, and any disturbance such as agitation, a sudden temperature change, or the introduction of a crystal of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, will cause it to assume its normal equilibrium conditions with the crystallization of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The other dotted curves of Fig. 68 have similar significances and represent experimentally observed metastable equilibria.

Metastable equilibria are of little industrial significance, but supersaturation is very commonly encountered. It may be produced in two ways. By the exclusion of all particles of solid solute the formation of

crystalline nuclei may be entirely prevented as described above. Another type of supersaturation may result from sudden changes of the conditions of a saturated solution even though crystallization has started and crystalline solute is present. This results from the fact that crystallization, especially in certain types of viscous solutions, is a slow process. Sudden cooling of such a solution will produce temporary conditions of supersaturation simply because the system is slow in adjusting itself to its equilibrium conditions. Agitation of the solution will hasten this adjustment.

In the majority of crystallization processes it is desirable to avoid supersaturation. Supersaturation of the type resulting from the absence of crystalline nuclei is prevented by *seeding* saturated solutions with crystals of solute. Spontaneous nucleus formation is also favored by the presence of rough, adsorbent surfaces. The crystallization of sugar on pieces of string to form rock candy and the scratching of the wall of a beaker to cause crystallization of an analytical precipitate are familiar illustrations of this principle. Supersaturation due to slow crystallization rates is avoided by using correspondingly slow rates of change of the conditions which promote supersaturation and in some cases by agitation. For these reasons it may generally be assumed that the normal solubility equilibria exist in industrial crystallization processes and that the saturated solutions possess their equilibrium concentrations.

DISSOLUTION PROCESSES

Problems arise in which it is desired to calculate the amount of solute which can be dissolved in a specified quantity of solvent or solution, or, conversely, the quantity of solvent required to dissolve a given amount of solute to produce a solution of specified degree of saturation. Where solvates are not formed in the system such calculations introduce no new difficulties. From the solubility data is determined the quantity of solute which may be dissolved in a unit quantity of solvent to form a saturated solution at the existing temperature. The amount of solute which may be dissolved in a solution is then the difference between the amount already present and the amount which may be present if the solution is saturated at the specified conditions, both quantities being based on the same quantity of solvent.

Illustration 2. A solution of sodium chloride in water is saturated at a temperature of 15°C . Calculate the weight of NaCl which can be dissolved by 100 lb of this solution if it is heated to a temperature of 65°C .

Solubility of NaCl at 15°C = 6.12 lb-mols per 1000 lb of H_2O .

Solubility of NaCl at 65°C = 6.37 lb-mols per 1000 lb of H_2O .

Basis: 1000 lb of water.

NaCl in saturated solution at 15° C = $6.12 \times 58.5 =$	358 lb
Percentage of NaCl by weight = $358/1358 =$	26.4%
NaCl in saturated solution at 65° C = $6.37 \times 58.5 =$	373 lb
NaCl which may be dissolved per 1000 lb of H ₂ O = $373 - 358 =$	15 lb
Water present in 100 lb of original solution = $100 \times (1.0 - 0.264) =$	73.6 lb
NaCl dissolved per 100 lb of original solution = $\frac{15 \times 73.6}{1000} =$	1.1 lb

It will be noted that the solubility of NaCl changes but very little with change in temperature.

Where the substance to be dissolved is a solvated compound the problem is complicated by the fact that both solute and solvent are added to the solution. Such calculations are best carried out by an algebraic method based on the equality of the total quantity of solute entering and leaving the process. Algebraic expressions are formed for the sum of the quantity of solute to be dissolved plus that originally present in the solution, and for the quantity of solute in the final solution. Since the total quantity of solute must be constant, these two expressions are equal and may be equated and solved. This method is demonstrated in the following illustration:

Illustration 3. After a crystallization process a solution of calcium chloride in water contains 62 lb of CaCl₂ per 100 lb of water. Calculate the weight of this solution necessary to dissolve 250 lb of CaCl₂ · 6H₂O at a temperature of 25° C. Solubility at 25° C = 7.38 lb-mols of CaCl₂ per 1000 lb of H₂O.

Basis: x = weight of water in the required quantity of solution.

$$\text{CaCl}_2 \cdot 6\text{H}_2\text{O to be dissolved} = \frac{250}{219} = \dots\dots 1.14 \text{ lb-mols}$$

$$\text{Total CaCl}_2 \text{ entering process} = 1.14 + \frac{62 \cdot x}{111 \cdot 100} = 1.14 + \frac{0.559x}{100} \text{ lb-mols}$$

$$\text{Total water entering process} = x + (1.14 \times 6 \times 18) = x + 123 \text{ lb}$$

$$\text{Total CaCl}_2 \text{ leaving process} = \dots\dots\dots 7.38 \frac{x + 123}{1000} \text{ lb-mols}$$

Equating:

$$1.14 + \frac{0.559x}{100} = 7.38 \frac{x + 123}{1000}$$

$$1140 + 5.59x = 7.38x + 908$$

$$1.79x = 232$$

$$x = 130 \text{ lb}$$

$$\text{Total weight of solution required} = 130 + (130 \times 0.62) = \dots\dots\dots 211 \text{ lb}$$

CRYSTALLIZATION PROCESSES

The crystallization of a solute from a solution may be brought about in three different ways. The composition of the solution may be changed

by the removal of pure solvent, as by evaporation, until the remaining solution becomes supersaturated and crystallization takes place. The second method involves a change of temperature to produce conditions of lower solubility and consequent supersaturation and crystallization. A third method by which crystallization may be produced is through a change in the nature of the system. For example, inorganic salts may be caused to crystallize from aqueous solutions by the addition of alcohol. Other industrial processes involve the *salting out* of a solute by the addition of a more soluble material which possesses an ion in common with the original solute. The calculations which are involved in this third type of crystallization processes are frequently very complicated and require a large number of data regarding the particular systems involved. Such systems involve more than two components and require application of the principles of complex equilibria which are discussed in a later section.

Calculations Where Solvates Are Not Formed. The most important crystallization processes of industry are those which combine the effect of increasing the concentration by the removal of solvent with the effect of change of temperature. Where crystallization is brought about only through change in temperature, the yields of crystals and the necessary conditions may be calculated on the basis of the quantity of solvent which remains constant throughout the process. From the solubility data may be obtained the quantity of solute which will be dissolved in this quantity of solvent in the saturated solution which will remain after crystallization. The difference between the quantity of solute originally present and that remaining in solution will be the quantity of crystals formed. Such problems may be of two types: one in which it is desired to calculate the yield of crystals produced by a specified temperature change; and the converse, in which the amount of temperature change necessary to produce a specified yield is desired. The percentage yield of a crystallization process is the percentage which the yield of crystallized solute forms of the total quantity of solute originally present.

Illustration 4. A solution of sodium nitrate in water at a temperature of 40°C contains 49% NaNO_3 by weight.

- a. Calculate the percentage saturation of this solution.
- b. Calculate the weight of NaNO_3 which may be crystallized from 1000 lb of this solution by reducing the temperature to 10°C .
- c. Calculate the percentage yield of the process.

Solubility of NaNO_3 at 40°C = 12.39 lb-mols per 1000 lb of H_2O .

Solubility of NaNO_3 at 10°C = 9.43 lb-mols per 1000 lb of H_2O .

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Basis: 1000 lb of original solution.

$\text{NaNO}_3 = 490 \text{ lb or } 490/85 = \dots\dots\dots$	5.77 lb-mols
Solvent water = $1000 - 490 = \dots\dots\dots$	510 lb
Molality of solution = $\frac{5.77}{510} \times 1000 = \dots\dots\dots$	11.31
a. Percentage saturation = $\frac{11.31}{12.39} = \dots\dots\dots$	91.5%
NaNO_3 in final saturated solution at $10^\circ \text{C} =$	
$\frac{510}{1000} \times 9.43 = \dots\dots\dots$	4.81 lb-mols
or $4.81 \times 85 = \dots\dots\dots$	409 lb
b. Yield of NaNO_3 crystals = $490 - 409 = \dots\dots$	81 lb
c. Percentage yield = $\frac{81}{490} = \dots\dots\dots$	16.5%

Illustration 5. A solution of sodium bicarbonate in water is saturated at 60°C . Calculate the temperature to which this solution must be cooled in order to crystallize 40% of the NaHCO_3 .

Solubility of NaHCO_3 at $60^\circ \text{C} = 1.96 \text{ lb-mols per } 1000 \text{ lb H}_2\text{O}$.

Basis: 1000 lb of H_2O .

NaHCO_3 in original solution = $\dots\dots\dots$	1.96 lb-mols
NaHCO_3 in final solution = $1.96 \times 0.60 = \dots\dots$	1.18 lb-mols

From the solubility data of NaHCO_3 it is found that a saturated solution containing 1.18 lb-mols per 1000 lb of H_2O has a temperature of 23°C . The solution must be cooled to this temperature to produce the specified percentage yield.

Calculations of the yields and necessary conditions of crystallization by concentration may be carried out by consideration of the quantity of solvent remaining after concentration has taken place. The quantity of solute which will be dissolved in this quantity of solvent in the saturated solution remaining after crystallization may be calculated from solubility data. The quantity of crystals formed in the process will be the difference between the quantity of solute originally present and that finally remaining in solution. If the concentration is accompanied or followed by a temperature change the problem is unchanged. It is only necessary to consider the final temperature in order to determine the quantity of solute remaining in solution. In such processes three variable factors are present: the yield, the temperature change, and the degree of concentration. Problems arise in which it is necessary to evaluate any one of these factors if the other two are specified.

Illustration 6. A solution of potassium dichromate in water contains 13% $\text{K}_2\text{Cr}_2\text{O}_7$ by weight. From 1000 lb of this solution are evaporated 640 lb of water. The remaining solution is cooled to 20°C . Calculate the amount and the percentage yield of $\text{K}_2\text{Cr}_2\text{O}_7$ crystals produced.

Solubility of $\text{K}_2\text{Cr}_2\text{O}_7$ at $20^\circ \text{C} = 0.390 \text{ lb-mol per } 1000 \text{ lb H}_2\text{O}$.

Basis: 1000 lb of original solution.

Water =	870 lb
$K_2Cr_2O_7$ =	130 lb
Water remaining after concentration = $870 - 640$ =	230 lb
$K_2Cr_2O_7$ in solution after crystallization at $20^\circ C$ =	
$\frac{230}{1000} \times 0.390 = 0.090$ lb-mol or 0.090×294 =	26.4 lb
Yield of $K_2Cr_2O_7$ crystals = $130 - 26.4$ =	103.6 lb
Percentage yield = $\frac{103.6}{130} =$	79.7%

Care must always be exercised that the true solvent in a crystallizing system is recognized. For example, in Fig. 66, curve *EB* represents conditions under which naphthalene is the solute and benzene the solvent. However, curve *EA* represents the solubility of benzene as *solute* in naphthalene as solvent. If a solution having a concentration of naphthalene less than that of point *E* is cooled to produce crystallization, pure benzene will crystallize as the solute and the naphthalene will be the solvent, remaining constant in quantity throughout the process. Similarly, in aqueous solutions of salts, if the concentration is less than the eutectic value, cooling will produce the crystallization of water as pure ice and the system may be treated as a solution of water in salt.

Illustration 7. A solution of sodium nitrate in water contains 100 grams of $NaNO_3$ per 1000 grams of water. Calculate the amount of ice formed in cooling 1000 grams of this solution to a temperature of $-15^\circ C$.

Concentration of saturated, water-in- $NaNO_3$ solution at $-15^\circ C$ = 6.2 gram-mols of $NaNO_3$ per 1000 grams of H_2O .

Basis: 1000 grams H_2O .

$NaNO_3$ in original solution =	100 grams
Per cent $NaNO_3$ by weight = $\frac{100}{1100} =$	9.1%

Basis: 1000 grams of original solution.

$NaNO_3$ = 91 grams or $91/85 =$	1.07 gram-mols
Water =	909 grams
Water dissolved in $NaNO_3$ in residual solution = $\frac{1000}{6.2} \times 1.07 =$	173 grams
Weight of ice formed = $909 - 173 =$	736 grams

Calculations Where Solvates are Present. Where solvates are involved it becomes necessary to consider the solvent chemically combined with the solute which is removed from solution when solvate crystals are precipitated or which is added to the solution when solvate crystals are dissolved. The calculations involved are most easily performed by establishing a weight balance for either component. A binary system of weight *W* containing *y* per cent component *A* and $100 - y$ per cent

component B will be considered. It is assumed that this solution separates under a given temperature change into two phases, phase 1 having a weight w_1 and a composition of y_1 per cent component A , and phase 2 having a weight $W - w_1$, and a composition of y_2 per cent component A . A weight balance of component A gives

$$yW = \quad (1)$$

$$\text{or} \quad \frac{w_1}{W} \quad (2)$$

In case separation results from evaporation of a weight component B , the weight balance of component A becomes

$$yW = y_1w_1 + y_2(W - w_1 - w_3) \quad (3)$$

Illustration 8. An aqueous solution of sodium sulphate is saturated at 32.5°C . Calculate the temperature to which this solution must be cooled in order to crystallize 60% of the solute as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

From Fig. 68 the solubility at 32.5° is seen to be 32.5% Na_2SO_4 .

Basis: 1000 lb of initial solution.

Na_2SO_4 crystallized = $325 \times 0.6 = 195$ lb

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallized = $195/0.441 = 442$ lb

Water in these crystals = $442 - 195 = 247$ lb

Water left in solution = $675 - 247 = 428$ lb

Na_2SO_4 left in solution = $325 \times 0.4 = 130$ lb

Composition of final solution = $130/(130 + 428) = 23.3\% \text{ Na}_2\text{SO}_4$

From Fig. 68 it is found that this concentration corresponds to a temperature of 27°C , the required crystallizing temperature.

Illustration 9. A solution of ferric chloride in water contains 11 lb-mols of FeCl_3 per 1000 lb of water. Calculate the composition and yield of the material crystallized from 1000 lb of this solution if it is so cooled as to produce the maximum amount of crystallization from a residual liquid.

From Fig. 67 it is seen that, if a solution of this composition is cooled, the hydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ will crystallize. The maximum crystallization from a liquid residue will result from cooling to the eutectic temperature, 27°C . Further cooling would cause complete solidification of the system. From Fig. 67 the solubility at the eutectic temperature is 13.3 lb-mols of FeCl_3 per 1000 lb of H_2O .

Basis: 1000 lb original solution.

$$\text{Percentage } \text{FeCl}_3 \text{ in original solution} = \frac{11 \times 162.2}{11 \times 162.2 + 1000} = 64.1\%$$

$$\text{Percentage } \text{FeCl}_3 \text{ in final solution} = \frac{13.3 \times 162.2}{13.3 \times 162.2 + 1000} = 68.3\%$$

$$\text{Percentage } \text{FeCl}_3 \text{ in } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = \frac{162.2}{162.2 + 108} = 60.0\%$$

Let x = pounds of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ crystallized.

$$\begin{array}{rcl}
 \text{Weight of FeCl}_3 & & \\
 \text{Original solution} & \text{Final solution} & \text{Crystals} \\
 (1000)(0.641) & = (1000 - x)(0.683) & + 0.600x \\
 \text{or} & x = 511 \text{ lb FeCl}_3 \cdot 6\text{H}_2\text{O crystals} &
 \end{array}$$

Illustration 10. An aqueous solution of ferric chloride contains 20 gram-mols of FeCl_3 per 1000 grams of water. Calculate the temperature to which this solution must be cooled in order to crystallize 60% of the FeCl_3 .

From Fig. 67 it is seen that at this concentration the crystals will be $\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$.

Basis: 1000 grams of water in the original solution.

FeCl_3 crystallized = $0.6 \times 20 = 12$ gram-mols

Water removed by crystals = $12 \times 2.5 = 30$ gram-mols or 540 grams

FeCl_3 remaining in solution = 8 gram-mols

Water remaining in solution = $1000 - 540 = 460$ grams

FeCl_3 remaining = $8 \times \frac{1000}{460} = 17.4$ gram-mols per 1000 grams water

This concentration is found from Fig. 67 to correspond to a temperature of 35.5°C .

Illustration 11. A solution of sodium sulphate in water is saturated at a temperature of 40°C . Calculate the weight of crystals and the percentage yield obtained by cooling 100 lb of this solution to a temperature of 5°C .

From Fig. 68 it is seen that at a temperature of 5°C the decahydrate will be the stable crystalline form. The solubilities read from Fig. 68 are as follows:

at 40°C : 32.6% Na_2SO_4

at 5°C : 5.75% Na_2SO_4

Basis: 100 lb of original solution, saturated at 40°C .

Percentage Na_2SO_4 in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals = $\frac{142}{142 + 180} = 44.1\%$

Let x = pounds of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals formed.

Weight balance of Na_2SO_4

$$\begin{array}{rcl}
 \text{Original solution} & \text{Final solution} & \text{Crystals} \\
 0.326(100) & = 0.0575(100 - x) & + 0.441x \\
 \text{or} & x = 69.5 \text{ lb Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O formed} &
 \end{array}$$

Weight of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in original solution = $32.6 \frac{322}{142} = 74 \text{ lb}$

Percentage yield = $\frac{69.5}{74} = 94\%$

Calculations from Line Segments of Equilibrium Diagrams. In the separation of crystals from a solution the weight ratio of the crystals to the weight of the original solution is given by Equation (2). Thus,

(4)

This ratio can be obtained directly from the line segments on a binary equilibrium diagram when compositions are plotted in weight per-

centage. This method is illustrated by Fig. 68 for the system Na_2SO_4 and H_2O . Starting with a homogeneous solution at a temperature t_1 containing y per cent Na_2SO_4 (component A), and cooling, crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (phase 1) will start to separate at a temperature t_2 . As the temperature drops crystallization will continue, the crystals having a uniform composition of 44.1% Na_2SO_4 corresponding to the decahydrate as represented by the upper boundary of this two-phase field. The percentage of Na_2SO_4 in the remaining liquid phase becomes progressively less as crystallization proceeds, and its decreasing composition will be represented by points on the solubility curve corresponding to the existing temperature. When the final temperature t_3 is reached the composition of the residual liquid will be represented by ordinate y_2 , where y_2 represents the percentage of component A (Na_2SO_4) in the liquid phase. The weight of the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals relative to the entire weight of the system as given by Equation (2) will be seen to be equal to the ratio of the line segments $y - y_2$ to $y_1 - y_2$ as shown above.

In general, the percentage by weight of any phase in a two-phase equilibrium mixture at a given temperature may be obtained from the equilibrium diagram by extending the concentration line across the field showing the phases present. The weight ratio of phase 1 to the total weight will then be the ratio of the line segment extending between the composition of the entire system and the composition of phase 2 to the line segment extending between the compositions of phases 1 and 2. Phase 1, represented by segment $y - y_2$, always corresponds to that phase which is richest in component A . For example, in the above system phase 1 represents the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystal phase for compositions above the eutectic and represents the liquid phase below the eutectic composition where ice separates as the solid phase.

Illustration 11 will be solved from line segments on the equilibrium diagram. By referring to Fig. 68 the value of y corresponding to saturation at 40°C is 32.6 per cent. At 5°C , the composition y_1 of the solid phase is 44.1 per cent, and that y_2 of the liquid phase is 5.75 per cent. Applying the above rule of segments the percentage weight of crystals separated is $\frac{32.6 - 5.75}{44.1 - 5.75} = 69.5$ per cent. By this ratio of segment lines the composition of any equilibrium mixture of two phases can be estimated from the equilibrium diagram.

It must be emphasized that the line-segment rule can be directly applied only when compositions are expressed in weight percentages and never when they are expressed in molality or mol fraction.

SOLUBILITIES IN COMPLEX SYSTEMS.
FRACTIONAL CRYSTALLIZATION

All the systems thus far discussed have contained only two primary components. Where three or more components are involved the solubility relationships become very complex because of the effect which the presence of each solute has on the solubility of the others. These mutual effects cannot be predicted without experimental data on the particular case under consideration. In the case of salts which are ionized in solution the following qualitative generalization applies: Where the same ion is formed from each of two ionized solute compounds, the solubility of each compound is diminished by the presence of the other. For example, the solubility of NaCl in water may be diminished by the addition of another solute which forms the chloride ion. This principle is applied in the crystallization of pure NaCl by bubbling HCl into concentrated brine. Similarly the solubility of NaCl in water is reduced by the addition of sodium hydroxide. This accounts for the recovery of nearly pure caustic soda by evaporation of cathode liquor in the electrolysis of sodium chloride.

The mutual solubility relationships in complex systems are of great importance in many industrial processes. Soluble substances frequently may be purified or separated from other substances by properly conducted *fractional crystallization* processes. In such processes conditions are so adjusted that only certain of the total group of solutes shall crystallize, the others remaining in solution. For the production of very pure materials it is frequently necessary to employ several successive fractional crystallizations. In such a scheme of recrystallization the crystal yield from one step is redissolved in a pure solvent and again fractionally crystallized to produce further purification.

Complete data have been developed for solubilities in many complex systems. The presentation and use by such data for more complicated cases are beyond the scope of a general discussion of industrial calculations. In an excellent monograph¹ by Blasdale the scientific principles involved in such problems are thoroughly discussed. Data for many systems are included in the International Critical Tables.

In Fig. 69 are the solubility data of Caspari² for the system of sodium sulphate and sodium carbonate in water, presented in an isometric, three-coördinate diagram. A diagram of this type permits visualization of the relationship existing in such systems of only three components. The solubility data determine a series of surfaces which, with the axial planes, form an irregular-shaped enclosure in space. Any conditions of

¹ "Equilibria in Saturated Salt Solutions," W. C. Blasdale (1927).

² Caspari, *Journal of the Chemical Society, London*, **125**, 2381 (1924).

concentration and temperature which fix a point lying within this enclosure correspond to a homogeneous solution. Points lying outside of the enclosure represent conditions under which at least one solid substance is present. The surfaces themselves represent conditions of equilibria between the indicated solids and saturated solutions. The line formed by the intersection of two of these surfaces represents conditions of equilibria between a mixture of two solid substances and saturated solution.

For example, curves *OABC* of Fig. 69 represent the solubility in water of Na_2SO_4 alone, corresponding to Fig. 68. The addition of Na_2CO_3 to such a system lowers the solubility of the Na_2SO_4 , as indicated by the

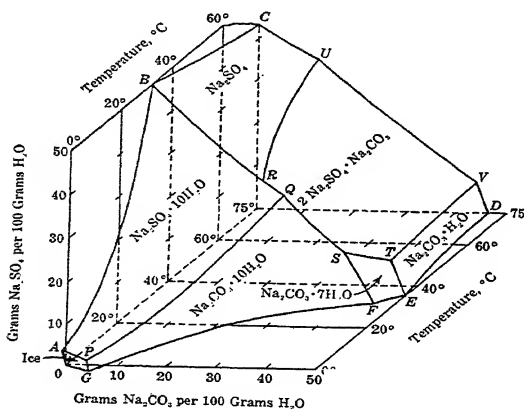


Fig. 69. Solubility of Sodium Carbonate-Sodium Sulphate in Water.

surfaces *ABRQP* and *BCUR*. The former surface corresponds to equilibria between crystals of pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and solutions containing both Na_2SO_4 and Na_2CO_3 . Surface *BCUR* represents similar equilibria with anhydrous Na_2SO_4 as the solid. Similarly, surface *GFSQP* represents equilibria between crystals of pure $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and solutions containing both Na_2CO_3 and Na_2SO_4 . These solutions are, therefore, saturated with respect to Na_2CO_3 but unsaturated with respect to Na_2SO_4 . If Na_2SO_4 were added to a solution whose conditions correspond to a point on surface *GFSQP*, the salt would dissolve and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ would crystallize.

The line *PQ* represents solutions which are saturated with both Na_2CO_3 and Na_2SO_4 . Such solutions are incapable of dissolving greater quantities of either salt and are in equilibrium with crystals of each.

It so happens that when crystals of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ are formed together in a solution, each solid compound is slightly soluble in the other, forming what are termed *solid solutions*. Therefore, line PQ represents equilibria between crystals of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ containing small amounts of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in solid solution, crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ containing small amounts of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in solid solution, and liquid solution containing both Na_2SO_4 and Na_2CO_3 .

At the higher temperatures the system is complicated by the decomposition of the hydrates and by the formation of a stable double salt of

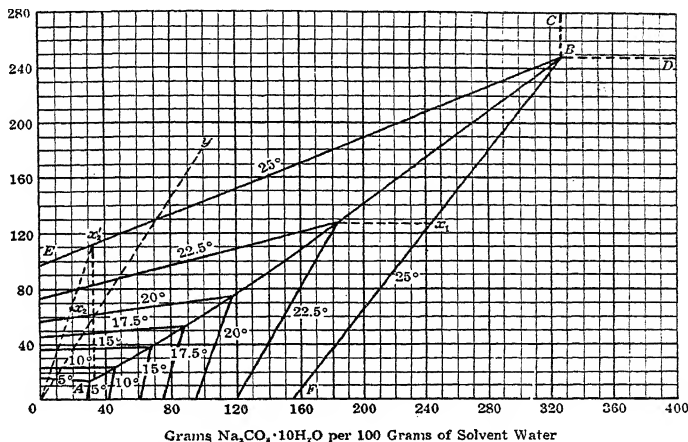


FIG. 70. Solubility Chart for the System $\text{Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ at Low Temperatures.

definite composition, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$. The surface *RQSTVU* represents equilibria between pure crystals of this double salt and liquid solutions. The other surfaces and lines of the diagram may be interpreted in a similar manner from the composition of the equilibrium solid which is marked on each surface.

An isometric diagram such as Fig. 69, though valuable as an aid to visualization, is not suitable as a basis for quantitative calculations. Data for such purposes are better presented as a series of isothermal solubility curves referred to only two axes as in Fig. 70. The coordinate units are the quantities of each of the *effective* solutes per unit quantity of *effective* solvent. In Fig. 70 the ordinates are the grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per 100 grams of *solvent* water, and the abscissas are grams of

10H₂O per 100 grams of effective solvent. This chart is useful only in the range of conditions in which these two compounds are the true, effective solutes. Each curve of Fig. 70 represents the solubility relationships, expressed in these units, at one indicated temperature. By interpolation between these curves solubilities at any desired temperature may be obtained. Points along curve *AB* represent conditions of saturation with both solutes. The curves running from the vertical axis to this curve represent solutions which are saturated with sodium sulphate but only partially saturated with sodium carbonate. Similarly, the curves running upward from the horizontal axis represent saturation with sodium carbonate. It will be noted that the solubility of each hydrated compound, expressed on the basis of a unit quantity of solvent water, is *increased* by the presence of the other. However, from Fig. 69, it was seen that the solubility of each of the anhydrous compounds is diminished by the presence of the other. This behavior results from the solvent action exerted by the water of hydration of each compound.

Point x_1 on Fig. 70 represents a composition which at a temperature of 25° C corresponds to a solution saturated with respect to sodium carbonate but unsaturated with respect to sodium sulphate. If such a solution is cooled, pure Na₂CO₃ · 10H₂O will crystallize and the composition of the residual solution will change along the dotted line. At a temperature of 22.5° C, corresponding to the intersection of this dotted line with curve *AB*, remaining solution will become saturated with both sodium carbonate and sulphate. Further cooling will result in crystallization of both Na₂CO₃ · 10H₂O and Na₂SO₄ · 10H₂O in crystals of the solid solutions which were previously discussed. The concentration of the residual solution will then diminish along curve *AB*. If cooling were stopped at 22.5° C a yield of pure Na₂CO₃ · 10H₂O crystals would be obtained, constituting a separation of one solute from the other.

Point x_2 on Fig. 70 represents a composition which at a temperature of 25° C corresponds to a solution unsaturated with respect to both solutes. If water is evaporated from such a solution at a temperature of 25° C the concentration of each solute will be increased. Since the relative proportions of the two solutes will remain unchanged, the composition of the solution will vary along a straight line passing through the origin of the diagram. If evaporation is continued a composition x_2' will be reached at which the solution is saturated with respect to sodium sulphate. Further evaporation will result in crystallization of pure Na₂SO₄ · 10H₂O, and the composition of the residual solution will vary along the 25° C isothermal line from x_2' to *B*. When the residual solu-

tion reaches a composition *B* it will be saturated with both solutes. Further evaporation will produce crystallization of both solutes, and the composition of the residual solution will remain unchanged at *B*. By such isothermal evaporation processes it is possible to separate the original solution into pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and a solution of composition *B* if the evaporation is not carried beyond the point of initial saturation with both solutes.

Points lying outside of a solubility isotherm on Fig. 70 represent the compositions of systems which at that temperature are heterogeneous mixtures. For example, at 25° C, any point lying in the field above curve *EBC* will represent a mixture of solid $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and a solution saturated with sodium sulphate but not with sodium carbonate. Similarly, a point in the field below *FBD* represents a system of solid $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and solution. A point in the field *CBD* corresponds to a system supersaturated with both $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. It will consist of a solution of composition *B* and a mixture of crystals of solid solutions of the two decahydrates.

With the aid of a chart of the type of Fig. 70 it is possible to carry out the calculations involved in crystallization problems by combined graphical and arithmetical means. If crystallization is produced by temperature change the quantity of effective solvent will remain constant throughout the process and may be used as the basis of calculation. The problem then resolves itself into one of finding the quantities of the solutes initially and finally associated with this basic quantity of solvent.

Illustration 12. An aqueous solution at a temperature of 22.5° C contains 21 grams of Na_2CO_3 and 10 grams of Na_2SO_4 per 100 grams of water.

a. Calculate the composition and weight of the crystals formed by cooling 1000 grams of this solution to a temperature of 17.5° C.

b. Repeat the calculation of part *a* to correspond to a final temperature of 10° C.

Basis: 1000 grams of original solution.

Percentage water by weight = $\frac{100}{131} =$	76.4%
$\text{Na}_2\text{CO}_3 = 7.64 \times 21 =$	160 grams
$\text{Na}_2\text{SO}_4 = 7.64 \times 10 =$	76.4 grams
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = 160 \times \frac{(106 + 180)}{106} =$	432 grams
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 76.4 \times \frac{(142 + 180)}{142} =$	173 grams
Solvent water = $1000 - (432 + 173) =$	395 grams
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ per 100 grams of solvent = $\frac{432}{395} =$	109 grams
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per 100 grams of solvent = $\frac{173}{395} =$	44 grams

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a. From Fig. 70 it is seen that cooling this solution to 17.5° C will produce crystallization of only pure $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

Composition of final solution at 17.5°.

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} =$	86 grams/100 grams solvent
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} =$	44 grams/100 grams solvent
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in final solution =	
$86 \times 3.95 =$	340 grams
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ crystallized = 432 - 340 =	92 grams

b. If the original solution is cooled to 10° C both Na_2CO_3 and Na_2SO_4 will crystallize.

Composition of final solution at 10° C.

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} =$	46 grams/100 grams solvent
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} =$	22 grams/100 grams solvent
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in final solution =	
$46 \times 3.95 =$	182 grams
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in final solution =	
$22 \times 3.95 =$	87 grams
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ crystallized = 432 - 182 =	250 grams
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallized = 173 - 87 =	86 grams

Where evaporation of solvent is involved in a crystallization process two types of problems may arise. It may be desired to calculate the quantity of solvent which must be removed in order to produce a specified yield of crystals or it may be desired to calculate the yield of crystals resulting from the removal of a specified quantity of solvent. In the first type of problem it is necessary to determine the composition of the solution remaining after the process. The quantity of solvent to be evaporated will then be the difference between that in the initial and final solutions. If both solutes crystallize in the process the residual solution will have a composition corresponding to saturation with both solutes at the final temperature. If only one solute crystallizes, the composition of the final solution may be determined graphically. From the specifications of the problem the relative proportions of the two solutes in the final solution will be fixed. This ratio between the two solutes will establish a straight line passing through the origin of the solubility chart, along which all solutions have the specified relative proportions of solutes. The point at which this line crosses the isothermal solubility curve corresponding to the final temperature conditions of the process will represent the composition of the final solution.

Illustration 13. An aqueous solution at a temperature of 25° C contains 95 grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and 21 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ per 100 grams of solvent water. Calculate the weight of water which must be evaporated from 100 lb of this solution in order to crystallize 60% of the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ if the final solution is cooled to 20° C

Basis: 100 lb of original solution.

Solvent water = $100 \times \frac{100}{216} =$	46.4 lb
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = 21 \times 0.464 =$	9.7 lb
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 95 \times 0.464 =$	44.0 lb
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in final solution = $44.0 \times 0.40 =$	17.6 lb
Ratio of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in final solution = $\frac{17.6}{9.7} =$	1.82

This ratio between the two solutes determines the dotted line *Oy* on Fig. 10. This line crosses the 20° C isothermal at a composition of 33.5 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and 61 grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per 100 grams of solvent water which is the composition of the final solution.

Solvent water in final solution = $17.6 \times \frac{100}{61} =$	28.8 lb
Water to be evaporated = $46.4 - 28.8 =$	17.6 lb

If a specified quantity of solvent is to be evaporated from a solution and it is desired to calculate the resultant yield of crystals, the composition of the entire final mixture of crystals and solution is readily determined by subtraction of the quantity of evaporated solvent. This composition corresponds to a point on the solubility chart. If the concentration of each solute is greater than that corresponding to saturation with both, the system is supersaturated with respect to both solutes and the residual solution must have the composition corresponding to complete saturation at the existing temperature. The quantity of each solute which will be crystallized will be the difference between the total amount present and that remaining in solution. If, in the final mixture, the concentration of only one of the solutes is greater than that corresponding to saturation, only this one *A* will be crystallized. The entire quantity of the other solute *B* must then be in the residual solution, fixing its composition with respect to this solute. The complete composition of the residual solution will be that corresponding to this concentration of solute *B* and saturation with solute *A* at the existing temperature. The quantity of solute *A* which will be crystallized will be the difference between the total quantity and that remaining in solution.

Illustration 14. A solution contains 160 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and 40 grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per 100 grams of solvent water. Water is evaporated from this solution and it is cooled to a temperature of 20° C. Calculate the weight and composition of the crystals formed from 100 lb of this solution, when:

- 10 lb of water are evaporated.
- 20 lb of water are evaporated.

Basis: 100 lb of solution.

$$\text{Solvent water} = 100 \times \frac{100}{300} = \dots\dots\dots 33.3 \text{ lb}$$

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = 0.333 \times 160 = \dots\dots\dots 53.3 \text{ lb}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 0.333 \times 40 = \dots\dots\dots 13.3 \text{ lb}$$

a. Solvent water in final solution = $33.3 - 10 = \dots\dots\dots 23.3 \text{ lb}$

Final mixture:

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ per } 100 \text{ lb solvent} = \frac{53.3}{0.233} = \dots\dots\dots 229 \text{ lb}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \text{ per } 100 \text{ lb solvent} = \frac{13.3}{0.233} = \dots\dots\dots 57 \text{ lb}$$

The point representing this composition on Fig. 70 is seen to correspond to supersaturation with Na_2CO_3 at 20°C but less than saturation with respect to Na_2SO_4 . Therefore, all the Na_2SO_4 must be in solution, and the residual solution will have a composition corresponding to 57 grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per 100 grams of solvent water and to saturation with $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ at 20°C .

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ per } 100 \text{ grams solvent in final solution} = 112 \text{ grams}$$

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ in final solution} = 112 \times 0.233 = \dots\dots\dots 26.2 \text{ lb}$$

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ crystallized} = 53.3 - 26.2 = \dots\dots\dots 27.1 \text{ lb}$$

b. Solvent water in final solution = $33.3 - 20 = \dots\dots\dots 13.3 \text{ lb}$

Final mixture:

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ per } 100 \text{ lb solvent} = \frac{53.3}{0.133} = \dots\dots\dots 400 \text{ lb}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \text{ per } 100 \text{ lb solvent} = \frac{13.3}{0.133} = \dots\dots\dots 100 \text{ lb}$$

The point representing this composition on Fig. 70 is seen to correspond to supersaturation with respect to both solutes at 20°C . The residual solution must, therefore, have the composition of complete saturation at 20°C .

Residual solution:

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ per } 100 \text{ grams solvent} = \dots\dots\dots 118 \text{ grams}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \text{ per } 100 \text{ grams solvent} = \dots\dots\dots 74 \text{ grams}$$

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ in residual solution} = 118 \times 0.133 = \dots\dots\dots 15.7 \text{ lb}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \text{ in residual solution} = 74 \times 0.133 = \dots\dots\dots 9.75 \text{ lb}$$

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ crystallized} = 53.3 - 15.7 = \dots\dots\dots 37.6 \text{ lb}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \text{ crystallized} = 13.3 - 9.75 = \dots\dots\dots 3.55 \text{ lb}$$

The system of sodium sulphate, sodium carbonate, and water has been selected as an illustration, not because of its industrial importance but because it exhibits most of the phenomena to be found in such ternary systems. Many other systems involve similar formations and decompositions of hydrates, double salts, and solid solutions and may be dealt with by means of similar diagrams and reasoning. Several systems of industrial importance show peculiarities of individual behavior which form the bases of important processes. For example, in the system $\text{NaNO}_3\text{-NaCl-H}_2\text{O}$ lowering the temperature decreases the solubility of NaNO_3 but *increases* that of NaCl in solutions which are saturated with both salts. This peculiarity makes it possible to crystallize pure

NaNO_3 by cooling a solution saturated with both salts. This principle is used on a large scale for the commercial production of Chilean saltpetre. In the system $\text{NaOH}-\text{NaCl}-\text{H}_2\text{O}$ the solubility of NaCl in solutions containing high concentrations of NaOH becomes very small. This fact is taken advantage of in the separation of NaCl from electrolytically produced NaOH solutions. The solution is merely concentrated by evaporation at a relatively high temperature where the solubility of NaOH is great. As the concentration increases NaCl crystallizes and solutions may be produced containing only traces of NaCl .

ENTHALPY — CONCENTRATION CHARTS OF SOLUTIONS

Recently W. L. McCabe¹ has called attention to the Merkel enthalpy concentration diagrams for binary solutions. In the Merkel chart the heat content per unit weight of solution is plotted against concentration for a series of constant-temperature lines. Once such a diagram of a given binary solution has been constructed, calculations of the heat effects involved in changing the concentrations and temperatures of the solution become simple and rapid and save the many calculations required in dealing with specific heats, concentrations, and heats of solution, at the various given temperatures. The Merkel chart has received extensive application in calculating the heat effects involved in mixing solutions, in multiple-effect evaporation, in absorption refrigeration, and in column rectification. The expenditure of the time required in constructing such a diagram is justified only in case of industrial specialization on a given system.

In constructing a heat content-concentration chart it is convenient to choose as a reference state the pure components at 0°C and 1.0 atmosphere. Since standard heats of solution and partial heats of solution are measured at 18°C it is convenient to establish the first heat content curve at this temperature and subsequently from this base line derive all other constant-temperature lines.

From Integral Heats of Solution. The following symbols represent heat contents at 18°C and 1 atmosphere pressure relative to the separate and pure components at 0°C and 1.0 atmosphere.

L_1 = heat content of solvent per unit weight of pure solvent at 18°C

L_2 = heat content of solute per unit weight of pure solute at 18°C

L = heat content of solution per unit weight of solution at 18°C

$-\Delta H_s = Q_s$ = integral heat of solution at 18°C per unit weight of solute for a solution containing w_1 units of solvent and w_2 units of solute

¹Trans. Am. Inst. Chem. Eng. **31**, 129-162 (1935).

From a heat balance,

$$(w_1 + \quad) = w_1 L_1 + w_2 L_2 + \quad \quad (5)$$

or

$$\quad \quad (6)$$

where

f_1, f_2 = weight fractions of solvent and solute, respectively, in the solution.

The relative heat content of the solution for other conditions of constant temperature may be calculated by adding the heat content above 18° C for solutions of different concentrations.

$$L_T = L_{18} + \int_{18}^T c_p dT \quad (7)$$

where

c_p is the heat capacity of the solution per unit weight of solution for a given concentration.

From Partial Heats of Solution. The heat content line at 18° C can also be calculated from partial heats of solution as discussed in Chapter VI, page 184. Thus,

$$(w_1 + w_2)L = w_1 L_1 + w_2 L_2 + w_1 \Delta \bar{H}_1 + w_2 \Delta \bar{H}_2 \quad (8)$$

or

$$L = f_1 L_1 + f_2 L_2 + f_1 \Delta \bar{H}_1 + f_2 \Delta \bar{H}_2 \quad (9)$$

where

$-\Delta \bar{H}_1 = \bar{Q}_1$ = partial heat of solution of the solvent per unit weight of solvent at 18° C

$-\Delta \bar{H}_2 = \quad$ = partial heat of solution of the solute per unit weight of solute at 18° C

The heat content lines at other temperatures are calculated as before.

In Fig. 71 is presented a heat content chart of hydrochloric acid in Btu per pound of solution, and in Fig. 72 a similar chart for sulphuric acid.

Illustration 15. Calculate the final temperature when 5.0 lb of 10% HCl at 60° F are mixed with 8 lb of 30% HCl at 100° F. From Fig. 71.

Heat content of 10% HCl at 60° F = (5) (-60) = -300

Heat content of 30% HCl at 100° F = (8) (-180) = -1440

Total heat content of mixture = -1740

Heat content per pound of final mixture $\frac{-1740}{13}$ = -134

Final concentration = $(0.5 + 2.4)/13 = 22.3\%$ HCl.

From Fig. 71 this heat content corresponds to a temperature of 90° F.

Heat content-concentration charts may also be expressed with reference to the solute present in a solution of infinite dilution at 0° C. Such a reference state has the advantage that solutions behave ideally at infinite dilution.

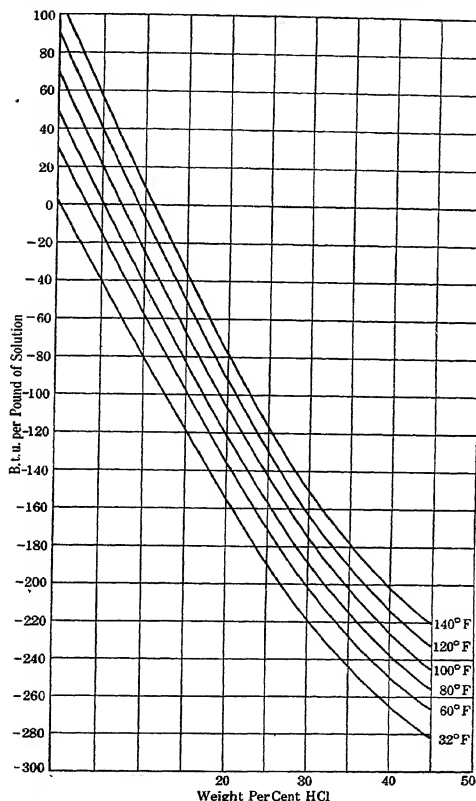


Fig. 71. Enthalpy-Concentration Chart of Hydrochloric Acid Solutions Relative to Pure HCl (*g*) and Pure H₂O (*l*) at 32° F. and 1 Atmosphere.

With this reference state the heat content L' per unit weight of solution at 18° C becomes

$$L' = f_1 L_1 + f_2 (\Delta H_s - \Delta H_\infty) + f_3 \bar{L}_2 \quad (10)$$

where

$-\Delta H_\infty$ = integral heat of solution of solute per unit weight of pure solute to form a solution of infinite dilution at 18° C.

Similarly, in terms of partial heats of solution

$$L' = f_1 L_1 + f_1 \Delta \bar{H}_1 + f_2 (\Delta \bar{H}_2 - \Delta \bar{H}_\infty) + f_2 \bar{L}_2 \quad (11)$$

To alter Fig. 71 to this new reference state $-f_2 \Delta H_\infty = f_2$ (829) Btu per lb is added to all values, where 829 is the integral heat of solution of pure HCl gas at 0° C dissolved in water to form a solution of infinite dilution at 0° C.

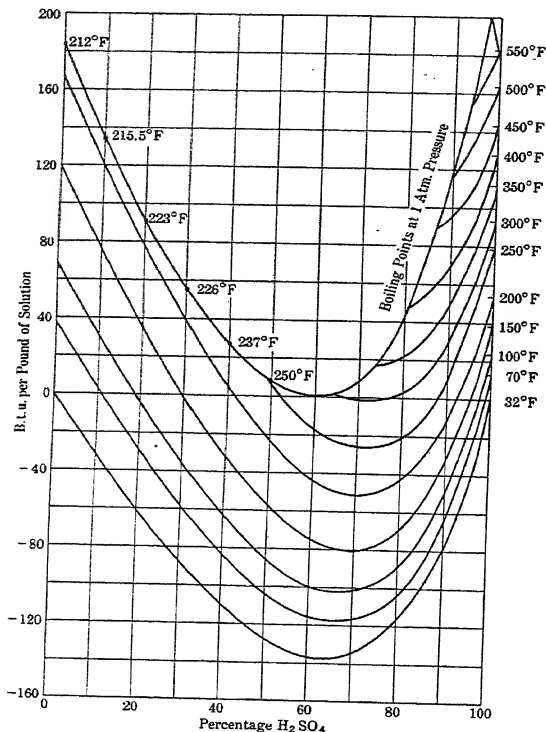


FIG. 72. Enthalpy-Concentration Chart of Sulphuric Acid Solutions in Water Relative to Pure Components (Liquid) at 32° F. and 1 Atmosphere Pressure.

SOLUBILITY OF GASES

When a gas is brought into contact with the surface of a liquid, some of the molecules of the gas striking the liquid surface will dissolve. These dissolved molecules of gas will continue in motion in the dissolved state, some returning to the surface and reëntering the gaseous state.

The dissolution of the gas in the liquid will continue until the rate at which gas molecules leave the liquid is equal to the rate at which they enter the liquid. Thus, a state of dynamic equilibrium is established and no further change will take place in the concentration of gas molecules in either the gaseous or liquid phase. The concentration of gas which is dissolved in a liquid is determined by the partial pressure of the gas above the surface.

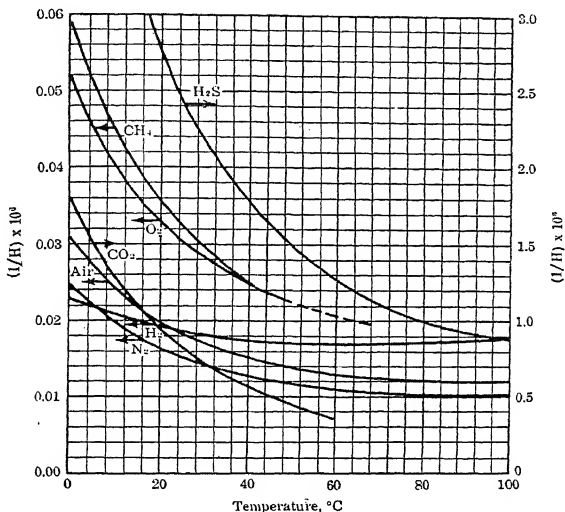


FIG. 73. Solubilities of Gases in Water. Variation of Henry's Constant, H , with Temperature (pressures in millimeters of mercury).

Henry's Law. The relationship between the concentration of gas dissolved in a liquid and the equilibrium partial pressure of the gas above the liquid surface is expressed by Henry's law. The ordinary statement of this law is that *the equilibrium value of the mol fraction of gas dissolved in a liquid is directly proportional to the partial pressure of that gas above the liquid surface.* Mathematically,

$$N_1 = \frac{1}{H} p_1$$

where

p_1 = equilibrium partial pressure of gas in contact with liquid

N_1 = mol fraction of gas in liquid

H = Henry's constant, characteristic of the system

This relationship has been found to be satisfactory at low concentrations, corresponding to low partial pressures of gas and high values of H . The factor H is a function of the specific nature of the gas and liquid and of the temperature, in general increasing with increase in temperature.

When pressures and concentrations are low the solubility data of a gas-liquid system are completely expressed by data relating values of Henry's constant, H , to temperature. In Fig. 73 are curves expressing this relationship for several common systems, the numerical values of $1/H$ corresponding to pressure in millimeters of mercury. The data for hydrogen sulphide and carbon dioxide will lead to considerable error if used for pressures above about 1 atmosphere. Similar data for many other systems of gases and liquids may be found in the International Critical Tables, Vol. III, page 254. These data permit calculation of solubilities under any condition in the range of their applicability.

Illustration 16. Calculate the volume of oxygen, in cubic inches, which may be dissolved in 10 lb of water at a temperature of 20° C and under an oxygen pressure of 1 atmosphere.

Solution:

From Fig. 73, for oxygen and water at 20° C, $1/H = \dots$	0.033×10^{-6}
Mol fraction of $O_2 = 760 \times 0.033 \times 10^{-6} = \dots$	25.1×10^{-6}
Mol fraction of water = \dots	1.000 —
Pound-mols of dissolved $O_2 = \frac{10}{18} \times 25.1 \times 10^{-6} = \dots$	13.9×10^{-6}
Volume of dissolved $O_2 = 13.9 \times 10^{-6} \times 359 \times \frac{293}{273} = \dots$	5.37×10^{-3} cu ft

or 9.3 cu in. measured at 20° C, and a pressure of 1 atmosphere.

Deviations from Henry's Law. Under conditions of high pressure or in the case of a gas of relatively high solubility the direct proportionality of Henry's law breaks down. Aqueous solutions of ammonia, carbon dioxide, and hydrochloric acid are examples of systems whose behavior deviates widely from that predicted by Henry's law except at low pressures. This deviation results in part from chemical reaction of the gas with the liquid and subsequent ionization of the dissolved molecules. Nernst has pointed out that Henry's law holds closely even for these cases when applied to the same single species in both phases, that is, to only the uncombined and unassociated molecules in the liquid phase. However, in general, experimentally determined data relating temperatures, pressures, and solubilities over the entire desired range are necessary in order to predict solubilities in such systems. These data are ordinarily expressed by *solubility isotherms* which relate the concentration of a dissolved gas to its partial pressure at a constant temperature. In Fig. 74 are solubility isotherms of ammonia in water at various temperatures. It will be noted that all the curves have considerable curva-

ture, and that those corresponding to the lower temperatures show points of inflection at high pressures. The form of the 20° C isotherm is typical of the behavior to be expected of a gas which is below its critical temperature and dissolved in a solvent with which it is miscible when in the liquid state. If measurements were continued at higher pressures the slope of the curve would be expected to increase, becoming asymptotic to the abscissa corresponding to a pressure of 6420 millimeters, the vapor pressure of liquid ammonia at 20° C. Gaseous ammonia at 20° C could not exist at higher pressures, and at this pressure an infinite amount of ammonia could be condensed and dissolved in 1

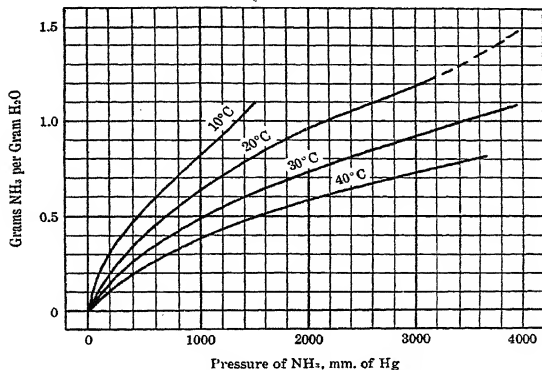


FIG. 74. Solubility of Ammonia in Water.

gram of water. The isotherms corresponding to higher temperatures should exhibit similar points of inflection if extended to higher pressures.

From the data of Fig. 74 it is apparent that Henry's law must be used with great care when dealing with a gas having a considerable affinity for the solvent or existing under high pressures. At high pressures the solubility calculated from Henry's law will, in general, be higher than the correct value. In such cases specific experimental data such as those of Fig. 74 are necessary for dependable calculations. Data for many systems, both in aqueous and organic solvents, are contained in the International Critical Tables (Vol. III, pages 255-283). Data are included on the solubilities of gases in solutions of other solutes as well as in pure liquids. In general, the solubility of a gas in a liquid is diminished by the addition of a non-volatile solute with which it does not react chemically.

Reversibility. Ordinarily the dissolution of a gas in a liquid may be considered as a completely reversible process. If the pressure of the gas is increased additional dissolution takes place. If the pressure is diminished gas will leave the solution and enter the gaseous phase. If the partial pressure of the solute gas is reduced to zero it would be expected that all the gas would be removed from the liquid. This condition is approached when a solution is boiled. As boiling is continued and the concentration of the solution of gas diminishes, the vapor above the surface of the liquid will become pure solvent, corresponding to a partial pressure of zero for the solute gas. However, in certain systems such as aqueous hydrochloric acid there is a small irreversible or residual solubility which persists even though the partial pressure of the gas be reduced to an immeasurable value. Even prolonged boiling will not remove all the HCl from an aqueous solution of hydrochloric acid. This, in general, is true of all solutions of gases where chemical combination, association, or ionization occurs.

ADSORPTION OF GASES BY SOLIDS

Certain solid substances exert strong attractive forces on the molecules of gases which are brought in contact with their surfaces. As a result, gases are adsorbed on such surfaces to form thin films of gas molecules in a condensed state. The solid substance is termed the *adsorbent* and the adsorbed material the *adsorbate*. The kinetic picture of this process on a plane surface is that a molecule of gas on striking certain unoccupied active spaces on the solid surface will be held there by the unbalanced attractive forces of the surface atoms of the solid. The exact origin and nature of these attractive forces are the subjects of much speculation. However, the union between the surface and an adsorbed molecule is not permanent and a continual evaporation takes place of adsorbed molecules which have acquired sufficient energy to break away from the surface forces. When a gas is brought into contact with an adsorbent surface, adsorption will take place until the rate at which gas molecules strike unoccupied active spaces and are adsorbed is equaled by the rate of evaporation of adsorbed molecules. No further change will take place in the concentration of the gas in either the adsorbed or gaseous phase, and a condition of dynamic equilibrium will exist.

The equilibrium between a gas and adsorbent is similar to that existing between a liquid and its vapor or between a solute gas and its solution. The amount of gas which is adsorbed to produce equilibrium conditions is a function of the partial pressure of the gas and the temperature, since these factors determine the rate at which molecules strike

the surface and the rate of evaporation of adsorbed molecules. Increase in pressure of the gas will result in greater adsorption. However, a solid surface is presumed to have only a definite number of active spaces upon which molecules may be adsorbed. When all such spaces are filled, further increase in pressure can cause no additional adsorption. On the basis of this type of reasoning Langmuir has developed a general equation to represent the relationship between the pressure and adsorbed quantity of a gas. This theory of adsorption is substantiated by considerable experimental evidence.

It is evident that only a very small quantity of gas, corresponding to a layer at most only a few molecules in thickness, can be adsorbed on a unit area of solid surface. However, adsorption becomes important when large surface areas are exposed, as in the case of finely divided powders or solids having porous structures. There is evidence that adsorbed gases are in a state of compression, producing a density greater than the normal density of the liquid state.

Capillary Condensation. Adsorbent materials of industrial importance are generally solid substances of porous structure which expose enormous interior surfaces. Activated charcoal, silica gel, and platinum black are examples of these materials. In such materials the type of adsorption described above is supplemented by what is known as *capillary condensation*. In the submicroscopic capillary pores of the solid the condensation of liquid will produce concave liquid surfaces of very small radii of curvature. It was pointed out in Chapter IV that the equilibrium vapor pressure of a liquid above a convex surface is greater than above a plane surface. Similarly, the equilibrium vapor pressure above a concave surface is *less* than the normal value. For this reason vapors which are under pressures much less than the normal saturation pressure may be caused to condense in very small capillaries, producing concave surfaces above which the equilibrium vapor pressure is abnormally low. Thus, if an adsorbent possesses submicroscopic capillarity it can not only adsorb vapors by means of surface attraction but also by condensation in its capillaries. The adsorbing capacity of such a material is much greater than for the same surface area having no capillary structure. Furthermore, increase in the pressure of the gas will continue to result in increased adsorption until all capillary spaces are filled. The smallest capillaries are filled with condensate at low pressures, and as the pressure is increased condensation progressively takes place in the capillaries of larger diameter. The relationship between pressure and adsorbed quantity is, therefore, dependent on the size distribution of the capillary pores as well as on the area of exposed surface and the nature of both adsorbent and gas.

Adsorption Isotherms. Data regarding adsorption equilibrium are ordinarily expressed as *adsorption isotherms* which relate quantities of adsorbate at equilibrium conditions to pressures at a constant temperature. A group of typical isotherms of various systems is presented in Fig. 75. Cubic centimeters of adsorbate gas, measured at 0° C and 760 millimeters of mercury, per gram of gas-free solid are plotted as ordinates, and pressures in millimeters of mercury as abscissas. It will be noted from these curves that adsorption is a specific behavior depending entirely on the nature of the system. Curves I and II are typical of the

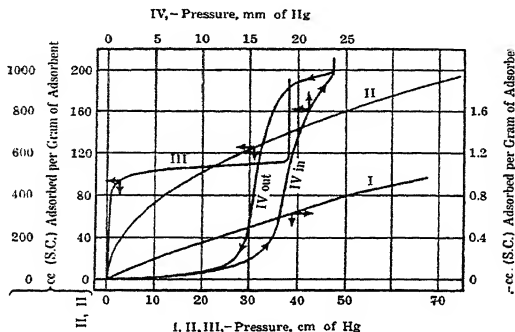


FIG. 75. Adsorption Isotherms.

- | | |
|---|---|
| <p>I. CO_2 on SiO_2 at 0° C.
Patrick, Preston, and Owens. J. Phys. Chem. 29, 421 (1925).</p> <p>II. SO_2 on SiO_2 at 30° C.
McGavack and Patrick. J. Am. Chem. Soc. 42, 946 (1920).</p> | <p>III. C_6H_6 on coconut charcoal at 59.5° C. Coolidge. J. Am. Chem. Soc. 46, 596 (1924).</p> <p>IV. H_2O on pine charcoal at 25° C. Allmand, Hand, Manning, and J. Phys. Chem. 33, 1682 (1929).</p> |
|---|---|

adsorption of a gas which is above its critical temperature or far removed from conditions of normal saturation. The adsorbed quantity increases with increased pressure but at a continually diminishing rate. Curve III is typical of the adsorption of a vapor below its critical temperature at pressures in the region of the normal vapor saturation pressure. When the pressure of the vapor is sufficiently increased to equal the normal vapor pressure of benzene at the existing temperature the vapor becomes saturated and normal condensation to the liquid state results. The adsorbed quantity in equilibrium with this pressure may be infinite.

Frequently the adsorption isotherm may be expressed by the empirical equation

$$a = k(p)^n$$

where

- a = equilibrium quantity of adsorbate
 p = partial pressure of adsorbate in vapor phase
 k, n = empirical constants

This equation is termed the Freundlich isotherm.

Reversibility of Adsorption: Stripping. Adsorption may ordinarily be looked upon as a completely reversible process. An adsorbed gas is evolved if its partial pressure in contact with the adsorbent is reduced below the equilibrium value. However, in certain cases, adsorption may be partly irreversible, indicating the formation of a definite compound between the adsorbent and the adsorbed material, and even though the pressure is reduced to zero a definite quantity of gas will remain adsorbed. The quantity of this residual or permanent adsorption is usually small and negligible in comparison to the quantities of adsorbate dealt with by commercial adsorbents. However, it may be of great importance, especially in the use of adsorbent materials as catalysts. The permanent adsorption of only minute traces of so-called "poisons" on such materials will ruin their catalytic properties.

Adsorbents are finding wide industrial use in the removal of various types of vapors from gas mixtures. The adsorbed vapors may be liberated and recovered or "stripped" in several different ways:

a. The temperature may be raised until the equilibrium pressure of the adsorbate exceeds atmospheric pressure. Adsorbate vapor will then be evolved and may be collected at atmospheric pressure.

b. The total pressure on the adsorbent may be reduced to a value below the equilibrium pressure. Adsorbed vapor may then be collected, undiluted, at this low pressure.

c. The adsorbent may be treated with a stream of gas in which the partial pressure of the adsorbate vapor is below the equilibrium pressure. Adsorbate vapors will be evolved in admixture with the gas. By using an easily condensed vapor for stripping, such as superheated steam, the adsorbed material may be easily recovered by condensing the stripping vapor only or by condensing the entire mixture and separating by decantation provided the two condensed vapors are immiscible.

d. The adsorbed vapors may be displaced by treatment with some other vapor which is preferentially adsorbed.

Adsorption Hysteresis. Curve IV on Fig. 75 indicates a behavior which is typical of certain adsorbents which possess a high degree of capillarity. As indicated by the arrows on the double section of the curve, the quantity adsorbed in equilibrium with a selected pressure is

dependent on the direction from which equilibrium is approached. If equilibrium is reached by the evolution of adsorbed material the upper or "out" curve is applicable. If the equilibrium conditions are reached by additional adsorption, with a continually increasing concentration, the lower or "in" curve applies. This behavior is known as *adsorption hysteresis* and is exhibited by many vapors when adsorbed in large quantities on silica gel and other capillary adsorbents. In calculations dealing with such systems data for both the "in" and "out" curves are frequently required.

Equilibrium Moisture Content. When water in the normal liquid state is brought into contact with a gas which is only partially saturated with water vapor, evaporation will take place as long as any liquid water remains. However, water which is held on a solid in an adsorbed state will not evaporate unless it is in contact with a gas in which the partial pressure of water vapor is less than the equilibrium adsorption pressure of the adsorbed water. For this reason a solid substance containing adsorbed moisture cannot be completely dried by exposure to gases which are partially saturated with water. The moisture content of the solid will merely be reduced until the equilibrium adsorption pressure is equal to the partial pressure of water in the gas. No further evaporation or drying can take place, even though the gas is far from normal saturation with water.

That portion of the moisture contained in a solid material which cannot be removed by exposure to gases which are partially saturated with water vapor is termed the *equilibrium moisture content*. The equilibrium moisture content of a substance is merely an exhibition of adsorption equilibrium and is equal to the quantity of water adsorbed by the substance in equilibrium with the partial pressure of water vapor existing in the surrounding gas. Equilibrium moisture content is, therefore, a function of the temperature and the partial pressure of water vapor in contact with the substance. These relationships may be expressed by equilibrium moisture content curves which are actually adsorption isotherms entirely similar to those of Fig. 75. Equilibrium moisture isotherms are ordinarily plotted against the percentage or relative humidity of the air. Such curves for a few important materials are plotted in Fig. 76. Similar data for other materials and at other temperatures have been determined by Wilson and Fuwa.¹

Equilibrium moisture content is of great importance in the industrial drying of porous, fibrous, or powdered materials such as textiles, soils, ceramic materials, vegetable tissue, and the like. No new concept is introduced if it is considered as an adsorption equilibrium.

¹ J. Ind. Eng. Chem. 14, 913 (1922).

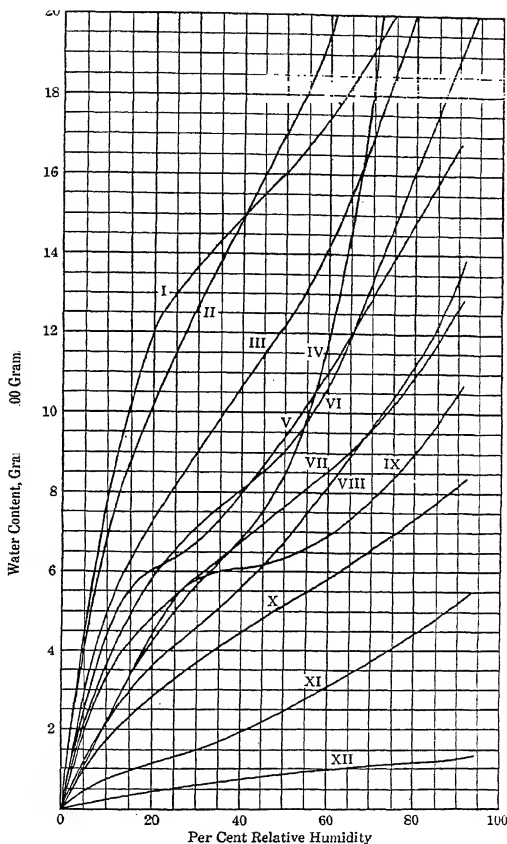


Fig. 76. Equilibrium Moisture Content at 25° C.

- I. Leather — Sole, Oak Tanned.
- II. Leather — Chrome Tanned.
- III. Wool — Worsted.
- IV. Soap — Ivory.
- V. Viscose.
- VI. Raw Silk.
- VII. Glue — Best Grade Hide.

- VIII. Cotton Cloth — Sheeting.
- IX. Sulphite Cellulose Pulp — Fresh, Unbleached.
- X. Bond Paper — "Manifest" Bond.
- XI. Cellulose Acetate Silk — Fibrous Form.
- XII. Kaolin — Florida.

Adsorption Calculations. If data for a family of isotherms corresponding to various temperatures are available, the equilibrium conditions of the system at any selected temperature and pressure may be estimated by interpolation. In Fig. 77 is such a group of isotherms from the data of Coolidge¹ for the adsorption of benzene vapors on activated charcoal. The adsorbed quantities, x , in cubic centimeters of vapor, measured at standard conditions, adsorbed per gram of gas-free or "outgassed" charcoal are plotted as ordinates. Logarithms of the pressures of benzene vapor in millimeters of mercury are plotted as abscissas. The logarithmic scale of pressures is desirable because of

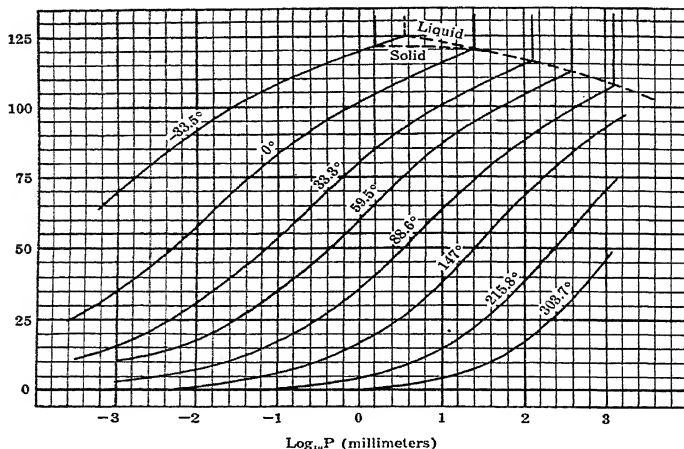


Fig. 77. Adsorption of Benzene on Activated Coconut Charcoal.
(Outgassed at 550° C.)

the wide range covered. The characteristic shape of these curves when plotted in linear coordinates is indicated by curve III of Fig. 75. The charcoal used in the experiments on which Fig. 77 is based was a coconut charcoal which had been outgassed by heating at 550° C under a reduced pressure.

It will be noted from Fig. 77 that the quantity of vapor adsorbed at equilibrium is increased by increase in pressure and diminished by increase in temperature. When the pressure is sufficiently increased to equal the normal vapor pressure of benzene at the existing temperature,

¹ J. Am. Chem. Soc. 46, 596 (1924).

the vapor becomes saturated and normal condensation to the liquid state results.

In the absence of experimental data the effect of temperature on the equilibrium adsorption of a vapor may be roughly predicted from its equilibrium vapor-pressure data. It has been found that in some cases the equilibrium quantity of vapor adsorbed at a specified relative saturation of the gaseous phase is but little affected by temperature. From this fact it follows that the equilibrium quantity of vapor adsorbed at a selected temperature and partial pressure is approximately equal to that adsorbed at any other temperature under such conditions of partial pressure that the relative saturation is the same as that of the first conditions. On the basis of this assumption it is possible to derive a set of isotherms from a single experimental curve.

Illustration 17. Using only the data of the 33° C isotherm of Fig. 77 and the vapor-pressure data of Fig. 3, page 72, estimate the quantity of benzene vapor adsorbed on activated charcoal at 215° C in equilibrium with benzene vapor under a partial pressure of 500 mm of Hg.

Solution:

Normal vapor pressure of benzene at 215° C = 14,000 mm

Relative saturation of benzene at 215° C, 500 mm of Hg

Normal vapor pressure of benzene at 33° C = 130 mm

Partial pressure of benzene at 33° C and relative saturation of 3.6% =

4.7 mm of Hg

Log 4.7 = 0.67

Adsorbed quantity at 33° C, 4.7 mm Hg = 94 cc, which is assumed to be equal to that adsorbed at 215° C and 500 mm of Hg.

On comparing the result of Illustration 17 with the experimentally observed values of Fig. 77 at 215° C it is seen that the estimate is high by over 50 per cent. From Fig. 77 it is apparent that the assumption on which these calculations are based is far from rigorously correct. If it were, the quantities adsorbed at normal saturation conditions, corresponding to a relative saturation of 1.0, would be constant. Actually these values are seen to diminish with increase in temperature. Calculations of the type of Illustration 17 are useful only for rough predictions of the order of magnitude of the effect of temperature change on adsorption.

The data of Fig. 77 are rigorously applicable only to the particular charcoal for which they were determined. The quantity adsorbed is entirely dependent on the source of the charcoal, the method of its preparation, and its subsequent treatment. The same limitation applies to all quantitative adsorption data. However, though such data are

rigorously applicable only to specific systems they may be used as a basis for approximate estimates of the general behavior of similar materials. Adsorption data for some systems are included in the International Critical Tables (Vol. III, page 249); a great many more are to be found in the very recent literature. Additional data are continually being determined.

When a particular adsorbent is to be used in an industrial process it is ordinarily desirable to obtain direct experimental data on the material in order to determine optimum operating conditions and designs. Such data may be obtained without great difficulty by various dynamic methods in which the quantity adsorbed in equilibrium with a gas stream of known composition is determined.

From a chart such as Fig. 77 complete prediction may be made of the equilibrium conditions in a system. Because of the rapid rate at which equilibrium is approached in industrial adsorption processes, it may generally be assumed that equilibrium conditions exist throughout.

Illustration 18. *a.* Estimate the number of pounds of benzene which may be adsorbed by 1 lb of the activated charcoal of Fig. 77 from a gas mixture at 20° C in which the partial pressure of benzene is 30 mm of Hg.

b. Calculate the percentage of this adsorbed vapor of part *a* which would be recovered by passing superheated steam at a pressure of 5 lb per sq in. and a temperature of 200° C through the adsorbent until the partial pressure of benzene in the steam leaving is reduced to 10.0 mm of Hg.

c. Calculate the residual partial pressure of benzene in a gas mixture treated with the freshly stripped charcoal of part *b* at a temperature of 20° C.

Solution: From Fig. 77.

a. C_6H_6 adsorbed at 20° C, 30 mm of Hg = 110 cc per gram
or $\frac{110}{22,400} \times 78 = 0.382$ gram per gram or pound
per pound

b. C_6H_6 adsorbed at 200° C, 10.0 mm of Hg = 20 cc per gram
Benzene recovered = 110 - 20 = 90 cc per gram
Percentage recovery = $\frac{90}{110} = \dots\dots\dots 82\%$

c. Pressure of benzene in equilibrium at 20° C with charcoal containing 20 cc of benzene per gram = antilog of 4.9 = 8×10^{-4} mm of Hg, the residual partial pressure of benzene.

For certain types of calculations it is convenient to express data in other forms than adsorption isotherms. An *adsorption isobar* relates the quantity adsorbed at equilibrium to temperature, at a constant pressure. An *adsorption isostere* relates the equilibrium temperature and pressure corresponding to a constant adsorbed quantity or concentration. Families of adsorption isobars or isosteres may be derived from a chart of isotherms such as Fig. 77. For industrial calculations it is usually desirable to express vapor concentrations on the basis of a unit quantity

of vapor-free gas and adsorbed quantities in weight or molal rather than volume units.

Preferential Adsorption. In Illustration 18 it was assumed that the presence of the gases from which the benzene was adsorbed had no effect on the equilibrium between the benzene vapor and the charcoal. This assumption is not necessarily rigorous because charcoal adsorbs considerable quantities of all the ordinary gases as well as benzene vapors. It would be expected that when charcoal is exposed to a mixture of gases a complicated equilibrium would be reached between each of the gases and its adsorbed quantity. Few quantitative data are available on the adsorption of mixtures of gases and vapors, but it is apparent that when several materials are adsorbed the presence of each must affect the equilibrium concentrations of the others.

It is an experimentally observed fact that, in general, adsorbent materials adsorb a gas of high molecular weight, high critical temperature and low volatility in preference to a gas of low molecular weight, low critical temperature, and high volatility. Such a preferentially adsorbed gas or vapor will displace other gases which have already been adsorbed. The chemical nature of the gas also plays an important part, but ordinarily it may be assumed that a heavy vapor of low volatility will almost completely displace a light gas of high volatility from an adsorbent. In the experiments of Coolidge on which Fig. 77 is based it was found that exposure of the outgassed charcoal to air before treatment with benzol vapors had no apparent effect on the final equilibrium.

In the absence of definite data it may ordinarily be assumed that when an adsorbent is treated with a vapor of low volatility such as water or benzene in admixture with a very volatile gas such as air, the adsorption of the gas will exert only a negligible influence on the normal equilibrium between the vapor and the adsorbent. When a gaseous mixture having several components of similar volatility is treated with an adsorbent, equilibrium quantities of all these components are adsorbed and general predictions of the equilibrium conditions cannot be made without specific data.

The preferential adsorptive properties which many substances exhibit are of great industrial importance in the selective separation of components of gaseous mixtures.

DISTRIBUTION OF A SOLUTE BETWEEN IMMISCIBLE LIQUIDS

When a solute is added to a system of two immiscible liquids, the solute is distributed between the liquids in such proportions that a definite equilibrium ratio exists between its concentrations in the two

phases. The equilibrium between the solute in the two phases is of a dynamic nature with solute particles continually diffusing across the interface from one liquid to the other. At equilibrium conditions the concentrations adjust themselves so that the rate of loss of solute particles by each phase is compensated by its rate of gain of particles from the other phase.

The equilibrium distribution of a solute between immiscible solvents is expressed by the *distribution coefficient*, K , which is the ratio of the concentrations in the two phases. Thus,

where C_A , C_B = concentrations of solute in phases A and B , respectively. If sufficient solute is present to saturate the system completely, each phase must contain solute in the concentration corresponding to its normal saturation conditions. Therefore, the distribution coefficient at saturation is merely the ratio of the solubilities of the solute in the two liquids.

Effect of Concentration. In ideal systems in which dissociation and association are absent the distribution coefficient is independent of concentration. Ordinarily, however, it shows marked variation with concentration, as indicated by the values in Table XVIII for the distribution of picric acid, $\text{HOC}_6\text{H}_2(\text{NO}_2)_3$, between water and benzene, C_6H_6 . Similar data for many other systems may be found in the International Critical Tables, Vol. III, page 418.

TABLE XVIII

DISTRIBUTION OF PICRIC ACID BETWEEN BENZENE AND WATER

C_A = concentration of $\text{HOC}_6\text{H}_2(\text{NO}_2)_3$ in water, gram-mols per liter of solution.
 C_B = concentration of $\text{HOC}_6\text{H}_2(\text{NO}_2)_3$ in benzene, gram-mols per liter of solution.
 K = distribution coefficient at 15–18° C = C_B/C_A .

C_B	K
0.000932	2.23
0.00225	1.45
0.01	0.705
0.02	0.505
0.05	0.320
0.10	0.240
0.18	0.187

Effect of Temperature. The effect of temperature on the distribution coefficient is generally small if the temperature coefficients of solubility are approximately equal in the two phases. In many cases the effect of temperature on distribution is entirely negligible, but in others

it may be very marked. Specific data are necessary in order to predict the effects of a temperature change. For many industrial calculations the effects of temperature changes of only a few degrees may be disregarded.

Distribution Calculations. The distribution of a solute between two immiscible liquids is of considerable industrial importance in the separation and purification of organic compounds. Ordinarily one liquid will be water or an aqueous solution and the other some immiscible organic solvent. Equilibrium concentrations of a solute in such systems may be varied by the addition of a second solute which is soluble in only one of the liquids. The addition of such a solute is, in effect, a change in the nature of one of the liquids.

From values of distribution coefficients equilibrium conditions are readily calculated.

Illustration 19. Picric acid exists in aqueous solution at 17° C in the presence of small amounts of inorganic impurities whose effects on its solubility may be neglected. The picric acid is to be extracted with benzene in which the inorganic materials are insoluble.

a. If the aqueous solution contains 0.20 gram-mol of picric acid per liter, calculate the volume of benzene with which 1 liter of the solution must be extracted in order to form a benzene solution containing 0.02 gram-mol of picric acid per liter. (Neglect the difference between the volume of a solution and that of the pure solvent.)

b. Calculate the percentage recovery of picric acid from the aqueous solution.

Basis: 1 liter of original aqueous solution.

Picric acid =	0.20 gram-mol
From Table XVIII, $K' = 0.505$ in final system =	C_B/C_A
Final concentration of picric acid in aqueous solution = $0.02/0.505$ =	0.0396 gram-mol per liter
Picric acid in final benzene solution = $0.20 - 0.0396$ =	0.16 gram-mol
Benzene required = $\frac{0.16}{0.02}$ =	8.0 liters per liter of aqueous solution
Percentage extraction of picric acid = $\frac{0.16}{0.20}$ =	80%

In calculations involving concentrated solutions the differences between the volume of a solution and that of the pure solvent cannot be neglected as was done in Illustration 19. In such cases it is most convenient to express the concentrations and distribution coefficients in terms of the weight of solute per unit weight of solvent. The units in which distribution data are ordinarily expressed, as in Table XVIII, may be readily converted into these terms if density-concentration data are available for both solutions.

If definite quantities of two immiscible solvents and a solute are mixed together, the final concentration of solute in either solution will be unknown. If the distribution coefficient varies considerably with concentration it will also be unknown. The distribution of the solute in such a case is best estimated by a method of successive approximations. A reasonable value of the final distribution coefficient is assumed as a first approximation. On the basis of this assumed value a first approximation to the final concentrations is calculated. The distribution coefficient is then corrected to correspond to these concentrations. On the basis of the second approximation to the distribution coefficient, a second approximation to the final concentrations is calculated. Unless the variation of distribution coefficient with concentration is very marked, two or three successive approximations of this type will yield results satisfactory for ordinary purposes.

Illustration 20. One liter of a benzene solution containing 0.10 gram-mol of picric acid per liter is agitated with 1.0 liter of water. Estimate the final concentration of picric acid in each solvent.

Solution: As a first approximation, assume from Table XVIII that the final distribution coefficient will be 0.5.

Let x_1 = gram-mols of picric acid in final benzene solution.

Picric acid in final aqueous solution = $0.10 - x_1$.

$$\frac{0.10 - x}{x} = 0.5$$

$$x_1 = 0.033$$

The distribution coefficient corresponding to this concentration is taken from the data of Table XVIII as a second approximation.

$$K_2 = 0.39$$

$$\frac{0.10 - x_2}{x_2} = 0.39$$

$$x_2 = 0.028$$

As a third approximation:

$$K_3 = 0.42 \text{ (corresponding to } C_B = 0.028)$$

$$x_3 = 0.029$$

This result may be taken as the final concentration of picric acid in the benzene solution. If greater accuracy is desired, more approximations should be carried out.

Picric acid in final benzene solution = 0.029 gram-mol

Picric acid in final aqueous solution = 0.071 gram-mol

PROBLEMS

1. A solution of sodium chloride in water contains 23.0% NaCl by weight. Express the concentration of this solution in the following terms, using data from Fig. 65.

a. Gram-mols of NaCl per 1000 grams of water (molality).

b. Mol fraction of NaCl.

- c. Gram-mols of NaCl per liter of solution at 30° C.
 - d. Pounds of NaCl per U. S. gallon of solution at 40° C.
2. An aqueous solution of sodium chloride contains 28 grams of NaCl per 100 cc of solution at 20° C. Express the concentration of this solution in the following terms, using data from Fig. 65.
- a. Percentage NaCl by weight.
 - b. Mol fraction of NaCl.
 - c. Lb-mols of NaCl per 1000 lb of water (molality).
 - d. Lb-mols of NaCl per U. S. gallon of solution at 0° C.
3. It is desired to prepare a solution of sodium chloride in water, having a molality of 2.00.
- a. Calculate the weight of sodium chloride which should be placed in a 1000-cc volumetric flask in order that the desired concentration will be obtained by subsequently filling the flask with water keeping the temperature of the solution at 30° C.
4. For the operation of a refrigerating plant it is desired to prepare a solution of sodium chloride containing 20% by weight of the anhydrous salt.
- a. Calculate the weight of sodium chloride which should be added to 1 gal of water at 30° C in order to prepare this solution.
 - b. Calculate the volume of solution formed per gallon of water used, keeping the temperature at 30° C.
5. a. A solution has a gravity of 80° Twaddell.
Calculate its specific gravity and its gravity in degrees Baumé.
b. An oil has a specific gravity at 60°/60° F of 0.651.
Calculate its gravity in degrees A. P. I. and degrees Baumé.
6. From the International Critical Tables, Vol. IV, plot a curve relating the solubility of sodium carbonate in water to temperature. Plot solubilities in ordinates, expressed in percentage by weights of Na_2CO_3 , and temperature as abscissas, expressed in degrees Centigrade, up to 60° C. On the same axes plot the freezing-point curve of the solution, or the solubility curve of ice in sodium carbonate, locating the eutectic point of the system.
- From Vol. III of the International Critical Tables plot density curves for sodium carbonate, similar to Fig. 65, at 0° C and 30° C. Plot densities in grams per cubic centimeter as ordinates and concentrations as abscissas, expressed in both percentage of NaCO_3 by weight and grams of Na_2CO_3 , per 100 cc of solution.
7. From the data of Figs. 66, 67, and 68 and Problem 6, tabulate in order the successive effects produced by the following changes:
- a. A solution of naphthalene in benzene is cooled from 20° to -10° C. The solution contains 0.6 gram-mol of naphthalene per 1000 grams of benzene.
 - b. A solution of sodium carbonate in water is cooled from 40° to -5° C. The solution contains 4.5 gram-mols of Na_2CO_3 per 1000 grams of water.
 - c. A mixture of aqueous sodium sulphate solution and crystals is heated from 10° to 60° C. The original mixture contains 3.3 gram-mols of Na_2SO_4 per 1000 grams of water.
 - d. Pure crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ are heated from 20° to 40° C.
 - e. A solution of FeCl_3 in water is cooled from 20° to -60° C. The solution contains 2.5 gram-mols of FeCl_3 per 1000 grams of water.

- f. A solution of FeCl_3 is evaporated at a temperature of 34°C . The original solution contains 5 gram-mols of FeCl_3 per 1000 grams of water, and it is evaporated to a concentration of 25 gram-mols of FeCl_3 per 1000 grams of water.
 - g. An aqueous solution of FeCl_3 is cooled from 45° to 10°C . The solution contains 18 gram-mols of FeCl_3 per 1000 grams of water.
8. In a solution of naphthalene in benzene the mol fraction of naphthalene is 0.12. Calculate the weight of this solution necessary to dissolve 100 lb of naphthalene at a temperature of 40°C .
9. An aqueous solution of sodium carbonate contains 5 grams of Na_2CO_3 per 100 cc of solution at 15°C . Calculate the pounds of anhydrous Na_2CO_3 which can be dissolved in 10 gals of this solution at 50°C .
10. A solution of sodium carbonate in water is saturated at a temperature of 10°C . Calculate the weight of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ crystals which can be dissolved in 100 lb of this solution at 30°C .
11. A solution of naphthalene in benzene contains 8.7 lb-mols of naphthalene per 1000 lb of benzene.
- a. Calculate the temperature to which this solution must be cooled in order to crystallize 70% of the naphthalene.
 - b. Calculate the composition of the solid product if 90% of the naphthalene is crystallized.
12. The concentration of naphthalene in solution in benzene is 1.4 lb-mols per 1000 lb of benzene. This solution is cooled to -3°C . Calculate the weight and composition of the material crystallized from 100 lb of the original solution.
13. A solution of naphthalene in benzene contains 25% naphthalene by weight. Calculate the weight of benzene which must be evaporated from 100 lb of this solution in order that 85% of the naphthalene may be crystallized by cooling to 20°C .
14. A solution of sodium carbonate in water is saturated at the temperature of maximum solubility, specific gravity, 1.368. Calculate the yield and percentage yield of solute crystals obtained by cooling 100 gal of this solution to 10°C .
15. A solution of sodium carbonate in water at 25°C contains 15 grams of Na_2CO_3 per 100 cc. This solution is evaporated at a temperature of 50°C .
- a. Calculate the number of pounds of water which must be evaporated from 10 gal of the solution in order that it will be saturated in the evaporator.
 - b. Calculate the weight of the crop of crystals which will be obtained by cooling the residue of the evaporation of part a to 15°C .
16. An aqueous solution of sodium carbonate contains 10% by weight of Na_2CO_3 . It is desired to crystallize out 90% of the sodium carbonate present by evaporation and cooling. The solution can be cooled to 10°C .
- a. Calculate the number of pounds of water which must be evaporated from 100 gal of this solution measured at 30°C .
 - b. Calculate the weight of the crop of crystals obtained from 100 gal of the original solution.
17. It is desired to recover 70% of the sodium carbonate contained in a solution having a concentration of 14.0 grams per 100 cc at 20°C . The solution is to be evaporated in a vacuum evaporator at a temperature of 60°C until the solution in the evaporator is saturated. Calculate the temperature to which this solution must be cooled in order to produce the required crystallization.

18. A solution of sodium carbonate in water contains 3.1 lb-mols of Na_2CO_3 per 1000 lb of water. In evaporating this solution 230 lb of water are removed at a temperature of 60°C per 1000 lb of original solution. Calculate the weight of crystals formed in the evaporation.

19. An aqueous solution of ferric chloride contains 12 lb-mols of FeCl_3 per 1000 lb of water. Calculate the yield of crystals formed by cooling 1000 lb of this solution to 28°C .

20. A solution of ferric chloride in water contains 15 gram-mols of FeCl_3 per 1000 grams of water.

a. Calculate the composition of the resulting crystals in percentage of each hydrate formed when this solution is cooled to 0°C .

b. Calculate the percentage of eutectic crystals present in the total crystal mass.

21. An aqueous solution contains 3.44% Na_2SO_4 and 21.0% Na_2CO_3 by weight. It is desired to cool this solution to the temperature which will produce a maximum yield of crystals of pure sodium carbonate decahydrate. Calculate the proper final temperature and the yield of crystals per 100 lb of original solution, using the data of Fig. 70.

22. It is desired to crystallize a maximum amount of pure $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ from the solution of Problem 21 by evaporating water at a temperature of 25°C . Calculate the quantity of water which must be evaporated and the yield of crystals produced per 100 lb of original solution.

23. A solution contains 25 grams of Na_2SO_4 and 4.0 grams of Na_2CO_3 per 100 grams of water. From 100 lb of this solution 20 lb of water are evaporated and the residual solution cooled to 20°C . Calculate the weight and composition of the crystals formed in the process.

24. Calculate the weight of water which must be evaporated from 100 lb of the solution of Problem 23 in order to crystallize 70% of the Na_2SO_4 as the pure decahydrate at a temperature of 15°C .

25. From the data of International Critical Tables plot a solubility chart similar to Fig. 70 for the system $\text{NaNO}_3\text{--NaCl--H}_2\text{O}$. Plot grams of NaNO_3 per 100 grams of water as abscissas and grams of NaCl per 100 grams of water as ordinates. Include the solubility isotherms for 15.5° , 50° , and 100°C .

26. A mixture of NaNO_3 and NaCl is leached with water at 100°C to form a solution which is saturated with both salts. From the chart of Problem 25, calculate the weight and composition of the crystals formed by cooling 100 lb of this solution to 15.5°C .

27. Assuming the applicability of Henry's law, calculate the percentage CO_2 by weight which may be dissolved in water at a temperature of 20°C in contact with gas in which the partial pressure of CO_2 is 450 mm of Hg.

28. Assuming the applicability of Henry's law, calculate the partial pressure of H_2S above an aqueous solution at 30°C which contains 3.0 grams of H_2S per 1000 grams of water.

29. Calculate the volume in cubic feet of NH_3 gas under a pressure of 1 atmosphere and at a temperature of 20°C which can be dissolved in 1 gal of water at the same temperature.

30. An aqueous solution of ammonia at 10°C is in equilibrium with ammonia gas having a partial pressure of 500 mm of Hg.

a. Calculate the percentage ammonia, by weight, in the solution.

b. Calculate the partial pressure of the ammonia in this solution if it were warmed to a temperature of 40°C .

31. Assuming that equilibrium quantities of adsorbate are determined only by the relative saturation of the adsorbate vapor, estimate the quantity of SO_2 adsorbed by the silica gel of Fig. 75 at a temperature of 10°C from a gas mixture in which the partial pressure of SO_2 is 150 mm of Hg. Vapor-pressure data may be obtained from Fig. 3, page 72.

32. Activated charcoal similar to that of Fig. 77 is to be used for the removal of benzene vapors from a mixture of gases at 20°C and a pressure of 1 atmosphere. The relative saturation of the gases with benzene is 83%.

- a. Calculate the maximum weight of benzene which may be adsorbed per pound of charcoal.
- b. The adsorbed benzene is to be removed by stripping with superheated steam at a temperature of 180°C . Calculate the final partial pressure to which the benzene in the steam leaving the stripper must be reduced in order to remove 90% of the adsorbed benzene.
- c. If the adsorbent is so used that the benzene-bearing gases always come into equilibrium with freshly stripped charcoal of part *b* before leaving the process, calculate the loss of benzene in these treated gases, expressed as percentage of the total benzene entering the process.

33. A solution of picric acid in benzene contains 30 grams of picric acid per liter. Calculate the quantity of water with which 1 gal of this solution at 18°C must be shaken in order to reduce the picric acid concentration to 4.0 grams per liter in the benzene phase.

34. One gallon of an aqueous solution of picric acid containing 0.15 lb of picric acid is shaken with 2 gal of benzene. Calculate the pounds of picric acid in each solute after the treatment.

35. Fifty pounds of unsized cotton cloth containing 20% total moisture are hung in a room of 4000-cu-ft capacity. The initial air is at a temperature of 100°F , at a relative humidity of 20%, and a barometric pressure of 29.92 in. of mercury. The air is kept at 100°F with no fresh air admitted and no air vented. Neglect space occupied by contents of room.

- a. Calculate the moisture content of the cloth and the relative humidity of the air at equilibrium.
- b. Calculate the equilibrium moisture content of cloth and corresponding relative humidity of the air if 100 lb of wet cloth instead of 50 lb are hung in the same room.
- c. What is the final pressure in the room under part *a*?

36. Calculate the heat evolved when 5 lb HCl gas at 80°F are dissolved in 20 lb of 10% HCl at 60°F , keeping final temperature at 60°F (Fig. 71).

37. Calculate the resultant temperature when 10 lb of water at 120°F are added to 10 lb of 40% HCl at 60°F (Fig. 71).

38. Calculate the heat required to concentrate 40 lb 5% HCl at 120°F to 8 lb 20% HCl at 120°F with the vapors leaving at 120°F (Fig. 71).

39. Calculate the final temperature when 100% H_2SO_4 at 60°F is diluted with a solution containing 10% H_2SO_4 at 100°F to form a solution containing 50% H_2SO_4 (Fig. 72).

CHAPTER XI

COMPRESSIBILITY OF GASES

The ideal gas law, as explained in Chapter III, permits satisfactory calculations of pressure-volume-temperature relationships at low pressures where the volumes per mol are relatively large and the distances between molecules great or where the temperatures are relatively high. However, under conditions of small molal volumes, corresponding to high pressures, the errors in assuming ideal gas behavior may be as great as 500%. Even at atmospheric temperature and pressure errors of 2-3% are encountered in the cases of some gases such as the heavier hydrocarbons.

Because of the great importance of high pressure processes numerous attempts have been made to develop accurate and generally applicable equations of state and graphical relationships. In this chapter are discussed those methods most suitable for industrial application.

Van der Waals' Equation. In the derivation of the simple kinetic theory, it is considered that each molecule has an available free space, in which it may move about, which is equal to the total volume occupied by the gas. This assumption is not correct except under such conditions that the volume of the molecules or particles themselves is negligible as compared to the total volume occupied by them. Actually, in each mol of gas there is a space of volume $(v-b)$ available for free motion, somewhat less than the total volume. The correction b by which the available free volume per mol differs from the total volume per mol is dependent on the volume actually represented by the N molecules themselves. It is this free volume which must be used in the more accurate derivation of the kinetic gas laws.

Another factor, neglected in the simple kinetic picture of a gas, is the force of attraction existing between molecules. The gas molecules next to a confining wall are subject to attractive forces tending to draw them toward the center of the mass of gas. As a molecule moves toward the wall, away from the main body of gas, work must be done against the attractive forces which tend to draw it back. As a result the kinetic energy of the molecule is transformed into potential energy and the impact against the wall is decreased. Decreasing the impacts of all molecules against the wall decreases the pressure exerted against it. It is

apparent then that a correction must be subtracted from the calculated pressure to compensate for this attractive effect. This correction will be proportional to the concentration of molecules per unit volume in the outer layer, which in turn is proportional to $1/v$. The correction is also proportional to the number of molecules in the interior of the gas which are near enough to act on the molecules in the outer layer. This number is also proportional to $1/v$. The total correction must be proportional to $1/v^2$. Then:

$$= p' - \frac{a}{v^2} \quad \text{or} \quad p' = p + \frac{a}{v^2}$$

where $p' =$ pressure calculated from the simple kinetic theory
 $p =$ actual pressure

The corrected equation then becomes:

(1)

This is the equation of van der Waals, which correctly represents the general form of the pressure-volume relationships of a gas, even when compressed to the region of liquefaction. Although this equation is a great improvement over the simple gas law, its numerical results represent only a fair approximation where molal volumes are small. The factors a and b are constants, characteristic of each gas, which are termed the van der Waals constants. These constants have been evaluated for many of the common gases and may be obtained from the data of the physical tables. In the first two columns of Table XIX are typical values corresponding to the expression of *pressures in atmospheres, volumes per gram-mol in cubic centimeters, and temperatures on the Kelvin scale.*

Actual Behavior of Gases at High Pressures. The behavior of a typical substance in the region of its critical point is graphically illustrated by those curves of Fig. 78 which are drawn with solid lines. Each curve represents the relationship between the pressure and the molal volume of carbon dioxide when isothermally compressed at the indicated temperature. The critical point is indicated by C . The double-crosshatched area represents the region of the liquid state of aggregation. The plain area is the region of the gaseous state. The single-crosshatched area represents a region in which both the liquid and gaseous states are present in equilibrium with each other. Thus, following along the 21.5°C experimental isothermal line from right to left, an increasing pressure is required to cause a reduction in volume until the *saturation curve, CB*, is reached. At this point the attractive

TABLE XIX

VAN DER WAALS' AND CRITICAL CONSTANTS OF GASES
From the data of the International Critical Tables.

a, b = van der Waals' constants. $a = (\text{atm}) \left(\frac{\text{cc}}{\text{g-mol}} \right)^2$; $b = \left(\frac{\text{cc}}{\text{g-mol}} \right)$

t_c = critical temperature, degrees C.

p_c = critical pressure, atmospheres.

d_c = critical vapor density, grams per cubic centimeter.

v_c = critical volume, cubic centimeters.

To convert values of a to $\frac{\text{lb}}{(\text{in.})^2} \left(\frac{\text{ft}^3}{\text{lb-mol}} \right)^2$ multiply values in table by 0.003776.

To convert values of b to $\left(\frac{\text{ft}^3}{\text{lb-mol}} \right)$ multiply values in table by 0.0160.

				p_c	d_c	
Argon.....	1.35×10^6	32.3	-122	48	0.531	75.2
Acetylene.....	4.37	51.2	36	62	0.231	113
Air.....	1.33	36.6	-140.7	37.2
Ammonia.....	4.19	37.3	132.4	111.5	0.235	72.4
Carbon dioxide...	3.60	42.8	31.1	73.0	0.460	95.5
Carbon monoxide.	1.46	39.4	-139	35	0.311	90.0
Chlorine.....	6.50	56.2	144	76.1	0.573	124
Ethylene.....	4.48	57.2	9.7	50.9	0.22	127
Hydrogen chloride	3.65	40.8	51.4	81.6	0.42	87
Hydrogen.....	0.245	26.6	-239.9	12.8	0.0310	64.5
Methane.....	2.25	42.8	-82.5	45.8	0.162	99
Methyl chloride...	7.50	65.1	143.1	65.8	0.37	137
Nitrogen.....	1.347	38.6	-147.1	33.5	0.3110	90
Oxygen.....	1.36	31.9	-118.8	49.7	0.430	74
Sulphur dioxide...	6.80	57.2	157.2	77.7	0.52	123
Water.....	5.48	30.6	374	217.7	0.4	45

forces between the molecules become sufficiently great to cause the beginning of aggregation into the liquid state. The volume may then be diminished without increase in pressure until the curve CA is reached. This curve represents the completion of condensation into the relatively incompressible liquid state. Further decrease in volume must be accompanied by large increases in pressure.

Van der Waals' Constants from Critical Data. The curves of Fig. 78 which are shown by broken lines represent the isothermal compression curves calculated from the van der Waals equation. It will be noted that the agreement between these curves and those experimentally determined is good at the higher temperatures. The great improvement offered by the van der Waals equation as compared with the simple gas law is indicated by the complete lack of agreement between the observed 57.8° C isothermal and that from the simple gas law plotted by a line of crosses.

At temperatures below the critical value it is seen that the van der Waals curve passes through a maximum and a minimum in the region of volumes where the experimentally observed curve becomes horizontal. It has been attempted to show that in this region the van der Waals curve represents the conditions which would

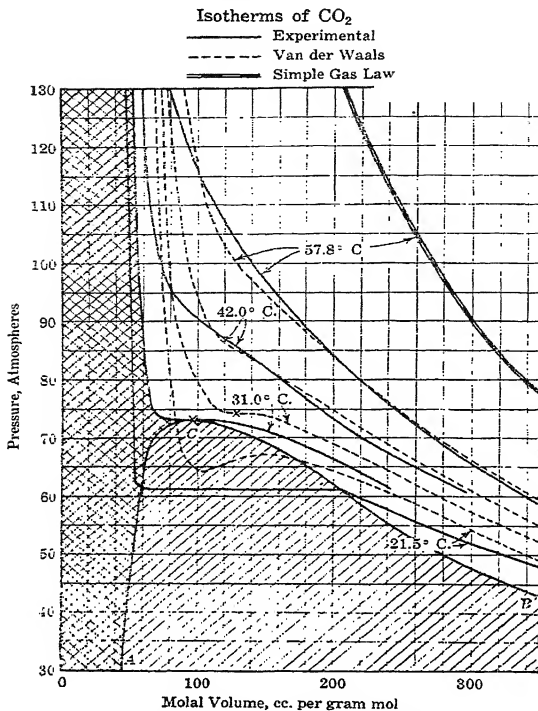


FIG. 78. Isotherms of Carbon Dioxide.

exist if condensation did not take place and the gas existed as a supersaturated vapor. For pressures lying between these maximum and minimum values the van der Waals equation has three real roots, or three different values of molal volume corresponding to each single pressure. For example, corresponding to a pressure p' are three values of volume:

$$v' = \alpha$$

$$v'' = \beta$$

$$v''' = \gamma$$

The factors of the equation are $(v - \alpha)$, $(v - \beta)$, and $(v - \gamma)$. Above the critical pressure the equation has but one real root, corresponding to only one value of volume for a given pressure. At the critical point the equation must have three real roots, but all three must be equal and correspond to a value of v which is equal to the critical volume v_c . Thus, at this point:

$$v' = v'' = v''' = \alpha = \beta = \gamma = v_c$$

Each of the three factors of the equation then is equal to $(v - v_c)$, and the equation itself is equal to the product of its factors $(v - v_c)^3$, which is equal to zero at the critical state.

Expanding:

$$(v - v_c)^3 = 0 \quad (2)$$

By expansion, van der Waals' equation becomes:

$$\left(\frac{RT}{p}\right)^3 - \frac{a}{p}v - \frac{av}{p} = 0 \quad (3)$$

At the conditions of the critical point Equations (2) and (3) must be identical and therefore the coefficients of the corresponding terms must be equal. For this reason:

$$(4)$$

$$= \frac{a}{p_c} \quad (5)$$

$$(6)$$

Dividing (5) by (6),

$$v_c = 3b \quad (7)$$

Substituting (7) in (5),

$$p_c = \frac{8a}{27b^2} \quad (8)$$

Substituting (7) and (8) in (4),

$$9b$$

or

$$= \frac{8a}{27bR} \quad (9)$$

Equations (7), (8), and (9) permit calculation of the critical data if the van der Waals constants are known. Solving (8) for a and substituting in (9),

$$T_c = \frac{8 \times 27b^2 p_c}{27bR} = \frac{8bp_c}{R} \\ RT_c \quad (10)$$

Substituting (10) in (8),

$$p_c = \frac{a \times 64p_c^2}{27 \times R^2 T_c^2} \\ 27 \times R^2 T_c^2 \quad (11)$$

By means of Equations (10) and (11) the van der Waals constants are calculated from experimentally observed values of the critical temperature and pressure. Because of the fact that the van der Waals equation is only a partially corrected approximation to the true equation of state, the constants a and b are not usually listed in the tables of physical data. However, the International Critical Tables list the critical data for a great variety of substances. From these critical data the corresponding van der Waals constants are readily calculated by the above equations. Care must be taken that consistent units are used for the values of R , T , and p_c .

Illustration 1. The International Critical Tables give the critical pressure of water as 217.7 atmospheres and the critical temperature as 374.0° C. Calculate the van der Waals constants.

Units: atmospheres, cubic centimeters per gram-mol, and degrees Kelvin.

$$R = 82.1$$

$$T_c = 374 + 273.1 = 647.1^\circ \text{K}$$

$$p_c = 217.7$$

Substituting in Equations (11) and (10):

$$a = \frac{27(0.821)^2 \times 10^4 \times (6.471)^2 \times 10^4}{6.4 \times 2.177 \times 10^3} = 5.48 \times 10^6$$

$$b = \frac{647.1 \times 82.1}{8 \times 217.7}$$

Van Laar's Rules. Two interesting rules have been formulated by van Laar concerning the additivity of the van de Waals constants. Van Laar found that the value of b for a chemical compound is equal to the sum of fundamental atomic values of b which are assigned to the component atoms. Thus, the fundamental atomic value of b for hydrogen in organic compounds is 3.14, and for carbon is 22.4. This atomic value of b for hydrogen is not the same as the value of b for hydrogen gas. The value of b for acetylene would then be $2 \times 22.4 + 2 \times 3.14 = 51.1$ which is in excellent agreement with the experimental value of 51.2 in Table XIV, page 383. Similarly, b for ethylene would be predicted to be $2 \times 22.4 + 4 \times 3.14 = 57.4$, which again is in excellent agreement with the value of Table XIX. The value of b for methane would be $22.4 + 4 \times 3.14 = 35.0$, much lower than that of Table XIX. This fact causes van Laar to question the accepted value of 45.8 as the critical pressure of methane and to offer the experimental data of two separate investigators, Wroblewski and Olzewski, who obtained values of 55 and 57 for the critical pressure. Using the mean value of 56 as the critical pressure of methane, the corresponding value of b is 34.9, in excellent agreement with the prediction of van Laar's rule. The calculated and experimental values of b are compared for a great variety of compounds, showing excellent agreement for the most part. Van Laar presents a complete table of fundamental atomic values of b for the elements from which the value of b for any compound may be estimated.

A similar rule of additivity is demonstrated for the square root of a . It is found that for a chemical compound the value of \sqrt{a} may be obtained as the sum of fundamental atomic values of \sqrt{a} which are assigned to the constituent atoms. This rule is not as general as that concerning the values of b . Several of the elements must be assigned different fundamental values of \sqrt{a} when in different types of compounds. Van Laar presents a table of atomic values of \sqrt{a} for the elements from which he predicts values of \sqrt{a} for a wide variety of compounds. These values for the most part show good agreement with the experimental data.

Van Laar's rules are of practical value when a material is encountered for which no experimentally determined critical data are available. From the rules it is possible to estimate the van der Waals constants. From these constants the critical temperature and pressure may be calculated from Equations (8) and (9). If one knows the critical temperature, the normal boiling-point may be estimated from Equation (5), Chapter IV, page 78.

¹ Zeit., f. anorg. u. allg. Chem. 104, 57-156 (1918).

"Zustandsgleichung," von Dr. J. J. van Laar, 1924, pp. 176-210.

Range of Usefulness of van der Waals' Equation. From the curves of Fig. 78, page 384, it is apparent that the van der Waals equation is far from an accurate representation of conditions in the neighborhood of the critical point. This fact is further emphasized by comparison in Table XIX of the observed and the calculated values of the critical volume which from Equation (7) should equal $3b$. For example, $3b$ for water is equal to 91.8, whereas the experimentally observed critical volume is 45. Therefore, it must be concluded that where very small molal volumes which approach the critical volume are encountered, the van der Waals equation is only a rough approximation. The accuracy of the equation where these small molal volumes are concerned generally increases with increasing temperature. From Table XIX it is seen that the critical gram-molal volumes are for the most part in the neighborhood of 100 cubic centimeters, increasing with the size of the molecule. In general then, the van der Waals equation cannot be depended upon for results of even fair accuracy where gram-molal volumes of less than 200 cubic centimeters are involved, except at temperatures well above the critical value.

In general the van der Waals equation may be used with a good degree of accuracy where molal volumes almost as low as the critical volume are involved if the temperature is well above the critical value. If the temperature is below the critical value, errors of the order of magnitude of 5 per cent may result from the use of the equation where the gram-molal volume is less than 2 or 3 liters. Water shows an extreme variation from the van der Waals equation as indicated by the great difference between v_c (45 cc) and $3b$ (92cc). The relative accuracies with which the various gases follow the equation may be estimated by comparisons of these two values. Carbon dioxide follows the equation much more closely than water as shown by the curves of Fig. 78 and by the fact that v_c is 96 cc, while $3b$ is 123 cc. From Fig. 78 it is seen that even at temperatures below the critical value the equation may be used where molal volumes are as low as 300 cc with errors of only about 5 per cent.

Use of the van der Waals Equation. Equation (1) may be written to apply to n mols of gas by multiplying both sides by n ,

$$\left(p + \frac{a}{v^2}\right)(nv - nb) = nRT \quad (12)$$

If V is the volume of the n mols of gas, $V = vn$.

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad (13)$$

This is the general form of the van der Waals equation, applicable to any quantity of gas. It is apparent that simple proportionalities cannot be derived from this equation and that molal volumes at the standard state are not the same for all gases.

By applying Equation (13) to two states and combining the resulting equations,

$$\frac{\left(p_1 + \frac{an^2}{V_1^2}\right)(V_1 - nb)}{\left(p_2 + \frac{an^2}{V_2^2}\right)(V_2 - nb)} = \frac{T_1}{T_2} \quad (14)$$

This equation may be used for determining any one of the conditions of temperature, pressure, or volume of state 2 if the other two and all the conditions of state 1 are known. However, n , the number of mols of gas involved, must be known. If this quantity is not specified it may be determined by applying Equation (13) to state 1. It will be noted that n appears in Equation (14) only in the coefficients of the correction terms. It is therefore permissible, where state 1 is such that very

large errors do not result, to use the simple gas law for determining an approximation to n which will be of sufficient accuracy for Equation (14). The solution of Equation (14) offers no particular difficulty if the unknown quantity is either pressure or temperature. If the volume is unknown the final equation becomes of cubic form and is best solved by the graphical method to be described later.

The general problem of determining the relationship between the weight, volume, temperature, and pressure of a gas is best solved by the direct use of Equation (13). From it may be determined, without difficulty, the pressure exerted by a specified quantity of gas at specified volume and temperature, or the temperature to which a specified quantity must be adjusted in order to exert a specified pressure in a specified volume. However, when either the volume V or quantity n is unknown the solution becomes mathematically difficult. A graphical approximation method may be used.

$$\text{Let} \quad \Delta = \left(p + \frac{n^2 a}{V^2} \right) (V - nb) - nRT \quad (15)$$

When the correct values for the terms of Equation (13) are introduced into Equation (15) the quantity Δ will equal zero. Equation (13) may be solved by assuming a series of values for the unknown quantity substituting them in Equation (15), and calculating the corresponding values of Δ . The assumed values of the unknown are then plotted as abscissas against the corresponding values of Δ as ordinates. The abscissa of the point at which this curve crosses the x -axis will be the correct value of the unknown.

Since the equation is of the cubic form there should be three correct roots for n and for V , although for conditions above the critical temperature two of these roots are imaginary. Below the critical temperature three real roots will be found, the largest value for V corresponds to the volume when entirely in the gaseous state, and the smallest value of V to the volume when entirely in the liquid state; similarly, the smallest value of n corresponds to the number of mols when entirely in the gaseous state.

The range of the values assumed for the unknown quantity in the graphical solution may be limited by first determining the value which it would have if the simple gas law applied. This value is then used as the first assumption and the corresponding value of Δ is calculated. Starting from this point a series of values is assumed such that, by each new assumption, the numerical magnitude of Δ , whether positive or negative, is decreased until it finally changes sign. These values are then plotted to as large a scale as convenient. In problems dealing with vapors close to liquefaction conditions it is always desirable to make sure that the value obtained by this graphical method actually is the largest real solution when V is the unknown or the smallest when n is the unknown. This verification may be carried out by continuing the curve relating Δ to the assumed values of V or n . For this continuation larger values of V or smaller values of n should be assumed. If the extended curve does not return to the x -axis the first solution is the proper one for use. If the curve does return to the x -axis, a new solution is represented by the abscissa of its intercept. This new solution should then be verified by still further continuation of the curve.

In using the van der Waals equation it is generally desirable to retain the system of units in which the constants are presented. The data of any particular problem may be readily converted to these units, whereas a change in the units of the equation becomes confusing because of the complicated form.

The following illustrations demonstrate the general methods of calculation.

Illustration 2. One hundred cubic feet of ammonia at a pressure of 14.6 lb per sq in. and a temperature of 20° C are to be compressed to occupy a volume of 9 cu ft at a temperature of 30° C. Calculate the pressure necessary.

Basis: 100 cu ft of NH_3 at the initial conditions.

Initial conditions:

Pressure: 14.6 lb per sq in. or $14.6/14.7 = 0.994$ atm

Volume: 100 cu ft or $100 \times 28.3 \times 10^3 = 2.83 \times 10^6$ cc

Temperature: 20° C or 293° K

Final conditions:

Volume: 9 cu ft or $9 \times 28.3 \times 10^3 = 0.255 \times 10^6$ cc

Temperature: 30° C or 303° K

Since the initial pressure is low, corresponding to a large molal volume, a good approximation to n , the number of mols of gas present, may be obtained from the simple gas law.

$$n \text{ (approx.)} = \frac{pV}{RT} = \frac{0.994 \times 2.83 \times 10^6}{82.1 \times 293} = 117 \text{ gram-mols}$$

From Equation (14):

$$p_2 = \frac{\left(p_1 + \frac{an^2}{V_1^2}\right)(V_1 - nb)T_2}{(V_2 - nb)T_1} - \frac{an^2}{V_2^2}$$

$$a = 4.19 \times 10^6 \quad b = 37.3$$

$$\frac{an^2}{V_1^2} = \frac{4.19 \times 10^6 \times (1.17)^2 \times 10^4}{(2.83)^2 \times 10^{12}} = \frac{4.19 \times 1.37 \times 10^{10}}{8.00 \times 10^{12}} = 0.717 \times 10^{-2}$$

$$\frac{an^2}{V_2^2} = \frac{4.19 \times 1.37 \times 10^{10}}{0.065 \times 10^{12}} = 0.882$$

$$nb = 117 \times 37.3 = 4360 = 0.0044 \times 10^6$$

$$(V_1 - nb) = (2.83 - 0.0044)10^6 = 2.83 \times 10^6$$

$$(V_2 - nb) = (0.255 - 0.0044)10^6 = 0.251 \times 10^6$$

$$p_2 = \frac{(0.994 + 0.007) \times 2.83 \times 10^6 \times 303}{0.251 \times 10^6 \times 293} - 0.882$$

$$= \frac{1.01 \times 2.83 \times 3.03}{0.251 \times 2.93} - 0.882 = 11.75 - 0.88 = 10.87 \text{ atm}$$

$$= 160 \text{ lb per sq in.}$$

If it were assumed that the simple gas law applied here the pressure calculated would be 168 lb, an error of +5.0%.

A shorter solution of this problem may be obtained by substituting the approximate value of n directly into Equation (15) for the final set of conditions obtaining a pressure of 157 lb per sq in. Such a procedure is less nearly accurate because of the error introduced by using the approximate value of n , whereas in the recommended method the approximate value of n is used only where it appears as a small correction difference from a large number and hence introduces only a slight error.

Illustration 3. Calculate the specific volume in cubic feet per pound of acetylene when under a pressure of 500 lb per sq in. at a temperature of 18° C.

Basis: 1 lb of C_2H_2 or 454 grams or $454/26 = 17.45$ gram-mols

$$a = 4.4 \times 10^5 \quad b = 51.2$$

$$p = 500/14.7 = 34.0 \text{ atm}$$

From the van der Waals equation:

$$\left[34.0 + \frac{(17.45)^2 4.4 \times 10^5}{V^2} \right] (V - 17.45 \times 51.2) = 82.1 \times 10^5$$

$$\left(34.0 + \frac{1.34 \times 10^9}{V^2} \right) (V - 900) = 4.16 \times 10^5$$

If the simple gas law applied:

Let $\left[34.0 + \frac{1.34 \times 10^9}{V^2} \right] (V - 900) = 4.16 \times 10^5$

Values of Δ are now calculated to correspond to assumed values of V , starting with $V = 12.2 \times 10^3$. These calculations are best tabulated. (In the column headings the single figures in parentheses refer to column numbers.)

1	2	3	4	5	6	7
V	$V - (0.9 \times 10^3)$	V^2	$\frac{1.34 \times 10^9}{V^2}$	$34.0 + (4)$	$(2) \times (5)$	$(6) - 4.16 \times 10^5$
12.2×10^3	11.3×10^3	1.49×10^8	9.0	43.0	4.86×10^5	+0.70
11.0×10^3	10.1×10^3	1.21×10^8	11.1	45.1	4.55×10^5	+0.39
10.0×10^3	9.1×10^3	1.0×10^8	13.4	47.4	4.31×10^5	+0.15
9.0×10^3	8.1×10^3	0.81×10^8	16.5	50.5	4.09×10^5	-0.07
8.0×10^3	7.1×10^3	0.64×10^8	20.9	54.9	3.90×10^5	-0.26

The values of Δ in column 7 are plotted in Fig. 79 against the assumed values of V in column 1. From the curve it is found that where Δ is zero, V is 9.3×10^3 cc. This value represents the solution of the equation.

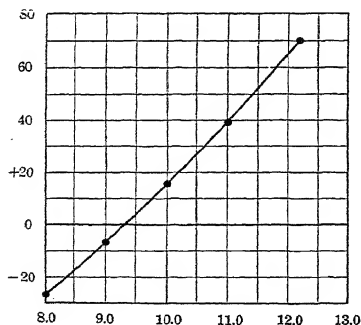


Fig. 79. Values of Δ

$$\begin{aligned} \text{Volume in cu ft} &= \frac{9.3 \times 10^3}{28.32 \times 10^3} \\ &= 0.328 \text{ cu ft} \end{aligned}$$

If n , the molal quantity, is the unknown, the solution is carried out in a similar manner.

Beattie-Bridgman Equation of State. Considerable discussion has been devoted to the van der Waals equation because of the fact that it represents a general relationship which may be applied, with accuracy sufficient for many purposes, to systems for which experimental compressibility data are not available. However, it is well recognized that for many requirements the van der Waals equation

is entirely inadequate and at best is only an improved approximation.

Many other equations of state have been proposed, some having theoretical significance, but many merely representing attempts to mathematically correlate

empirical data. One of the most noteworthy of these equations is that of Beattie and Bridgman.^{1, 2} The Beattie-Bridgman equation contains five constants which must be empirically determined for each particular gaseous system to which it is applied. However, the equation is unique because of the relative ease with which these constants may be evaluated from a limited amount of experimental data. The methods for evaluating the constants are discussed by Beattie and Bridgman in the papers cited above and also by Deming and Miss Shupe.³ The equation is as follows:

where a, b, A_0, B_0, c = empirically determined constants
 v = molal volume, liters per gram-mol
 p = pressure, atmospheres
 T = temperature, °K
 R = gas law constant = 0.08206

In Table XX are values of the constants of Equation (16) for several common gases. These constants were evaluated by Beattie and Bridgman⁴ and correspond to the above units. Similar data for other systems are being evaluated and may be found in the current literature.

TABLE XX
BEATTIE-BRIDGMAN CONSTANTS

Gas	A_0	a	B_0	b	c	Temp. range °C	Mini- mum v cc/g- mol
He	0.0216	0.05984	0.01400	0.0	0.004×10^4	400 to -252	100
H ₂	0.1975	-0.00506	0.02096	-0.04359	0.0504×10^4	200 to -244	100
N ₂	1.3445	0.02617	0.05046	-0.00691	4.20×10^4	400 to -149	180
O ₂	1.4911	0.02562	0.04624	0.004208	4.80×10^4	100 to -117	110
Air	1.3012	0.01931	0.04611	-0.01101	4.34×10^4	200 to -145	125
CO ₂	5.0065	0.07132	0.10476	0.07235	66.00×10^4	100 to 0	180
CH ₄	2.2769	0.01855	0.05587	-0.01587	12.83×10^4	200 to 0	166

In the ranges of temperature and molal volume indicated in the table, the equation was found to yield an average deviation of only 0.18 per cent from the accepted experimental values.

Equation (16) and the constants of Table XX may be used to calculate accurately pressure, volume, temperature relationships over wide ranges of conditions. Such an equation is of great value for the extrapolation of limited experimental data and for highly precise interpolation between observed values. It is also valuable in thermodynamic calculations because of the fact that it completely expresses compressibility data in a rigorous equation which may be incorporated in any desired mathematical operations. Its use in direct compressibility calculations is cumbersome, but once the constants are evaluated for a particular gas a complete set of compressibility charts such as Figs. 80, 81, and 82 may be constructed and conveniently used in the manner described in the following sections.

¹ J. Am. Chem. Soc. **49**, 1665 (1927).

² Idem, **50**, 3133 (1928).

³ J. Am. Chem. Soc. **52**, 1382 (1930); **53**, 843, 860 (1931).

⁴ Idem, **50**, 3133 (1928).

COMPRESSIBILITY FACTOR

The equation of state may be written,

$$pV = CnRT \quad (17)$$

where C is termed the *compressibility factor* and is a function of pressure, temperature, and the nature of the gas. If values of the compressibility factor of a gas are known, all calculations involving its p - V - T relationships may be carried out by simple proportionalities derived from Equation (17). Thus, applying Equation (17) to a gas at two different conditions and combining the resulting equations,

From Equation (18) can be made accurately all the types of calculations which were carried out approximately with the simple gas law. The correct normal molal volume is equal to $C_s \times 359$ cubic feet per pound-mol or $C_s \times 22.41$ liters per gram-mol, where C_s is the compressibility factor at standard conditions. With a knowledge of compressibility factors it thus is possible to extend the entire system of calculation which was used with the simple gas law to apply at any desired conditions of temperature or pressure. The simple gas law may be considered as representing a special case in which the compressibility factor is equal to unity. The introduction of factors other than unity does not appreciably complicate the use of the expression.

The nature of the variation of the compressibility factor C with pressure, molal volume, and temperature is shown by the curves of Figs. 80, 81, and 82 for nitrogen. In the range covered by these three charts the compressibility factor of nitrogen may be found at any specified conditions by interpolating on the proper chart. If the pressure and temperature are specified the compressibility factor is read from Fig. 80. If the molal volume and temperature or the pressure and molal volume are specified, Fig. 81 or Fig. 82 is used.

The use of compressibility factor data is demonstrated by the following illustrations, dealing with nitrogen.

Illustration 4. One cubic foot of nitrogen at a temperature of 50°C and a pressure of 30 atmospheres is compressed to a pressure of 60 atmospheres and cooled to a temperature of -50°C . Calculate the final volume.

The compressibility factors at the initial and final conditions may be obtained from Fig. 80.

Initial conditions:

$$\begin{aligned} p_1 &= 30 \text{ atm} \\ V_1 &= 1.0 \text{ cu ft} \\ T_1 &= 50^\circ\text{C} = 323^\circ\text{K} \\ C_1 &= 1.001 \end{aligned}$$

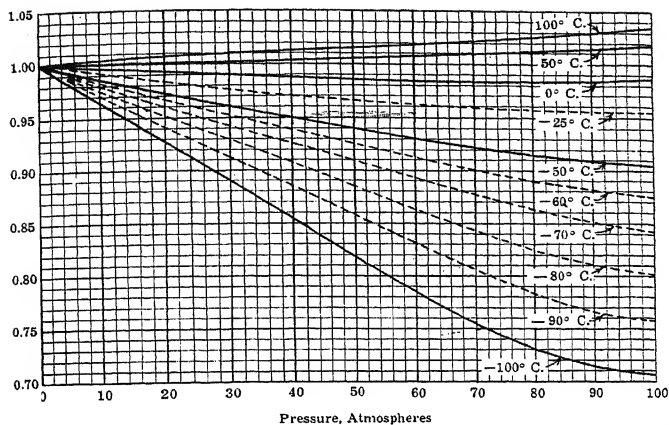


FIG. 80. Compressibility Factors of Nitrogen Corresponding to Specified Pressures and Temperatures.

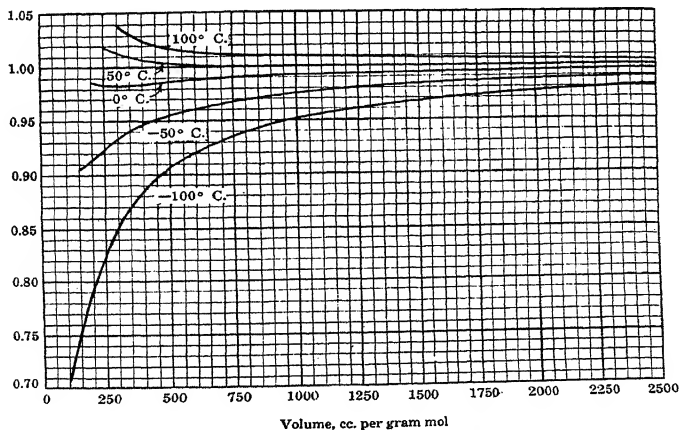


FIG. 81. Compressibility Factors of Nitrogen Corresponding to Specified Molal Volumes and Temperatures.

Final conditions:

$$\begin{aligned} p_2 &= 60 \text{ atm} \\ T_2 &= -50^\circ \text{C} = 223^\circ \text{K} \\ C_2 &= 0.930 \end{aligned}$$

From Equation (18)

$$\frac{30 \times 223 \times 0.930}{60 \times 323 \times 1.001} = 0.321 \text{ cu ft}$$

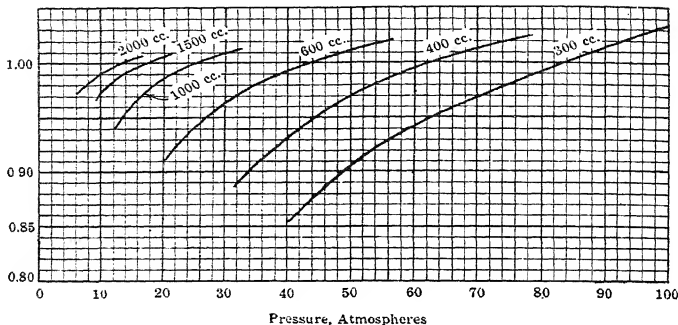


FIG. 82. Compressibility Factors of Nitrogen Corresponding to Specified Pressures and Molal Volumes.

Illustration 5. Calculate the pressure in pounds per square inch to which nitrogen must be compressed in order that 1.0 kg at a temperature of 50°C may be contained in a cylinder having a volume of 10 liters.

From Fig. 80 it is found that C_s , the compressibility factor of nitrogen at standard conditions, is equal to 0.999. The volume of 1.0 kg or 35.7 gram-mols of nitrogen at standard conditions is then $0.999 \times 35.7 \times 22.41$ or 801 liters.

Final conditions:

$$\begin{aligned} v &= \text{molal volume} = 10/35.7 = 0.28 \text{ liter} \\ T &= 323^\circ \text{K} \\ C &= 1.015 \text{ (from Fig. 81)} \end{aligned}$$

From Equation (18), page 392

$$\begin{aligned} p_2 &= p_1 \frac{V_1 \times T_2 \times C_2}{V_2 \times T_1 \times C_1} \\ &= \frac{801 \times 323 \times 1.015}{10 \times 273 \times 0.999} \end{aligned}$$

Illustration 6. A steel cylinder having a volume of 5 liters contains 400 grams of nitrogen. Calculate the temperature to which the cylinder may be heated without the pressure exceeding 50 atmospheres.

$$\begin{aligned} \text{Mols of nitrogen} &= 400/28 = 14.30 \text{ gram-mols;} \\ \text{Molal volume} &= 5000/14.30 = 350 \text{ cc} \\ p &= 50 \text{ atm} \\ C &= 0.945 \text{ (estimated from Fig. 82)} \\ R &= 82.1 \end{aligned}$$

From Equation (17):

$$T = \frac{50 \times 350}{82.1 \times 0.945} = 225^\circ \text{K or } -48^\circ \text{C}$$

The construction of compressibility curves is justified only if extensive and numerous calculations are required dealing with some particular gas. For isolated problems it is more convenient to use a suitable equation of state or to take data directly from critical tables as described in the next paragraph.

Empirical Compressibility Factors. A large amount of experimental work has been carried out on the more common and industrially important gases. The results may be found in the original literature and in the more extensive physical tables. In the International Critical Tables are experimental data for many gases and extensive references to the literature.

Experimental compressibility data are commonly presented in tables or curves showing values of the product pV at various values of p for constant values of T where the product is taken as 1.0 at 1 atmosphere pressure and 0°C . These data are arranged to show the isothermal variation of pV with pressure. If C_s is the compressibility factor of the gas at 0°C and 1 atmosphere pressure then the compressibility factor of the gas for any other condition may be obtained from Equation (29):

$$C = C_s(pV) \frac{273}{T} \quad (19)$$

The value of C_s is nearly unity for the common gases. It may be obtained accurately from density measurements made at standard conditions from the relation

$$C_s = \frac{M}{d_s 22.41}$$

where M is the molecular weight and d_s is the density in grams per liter at 0°C and 1 atmosphere pressure.

The compressibility factor of all gases is unity when the pressure is zero. Thus, values of C_s may also be obtained by plotting the values of pV against p at 0°C and extrapolating the graph to $p = 0$.

Then $C_s = \frac{p_s V_s}{p_0 V_0}$ where $p_0 V_0$ is the extrapolated value of pV at $p = 0$.

Compressibility factors may be calculated from Equation (19) and plotted against the corresponding pressures to obtain a chart of the form of Fig. 80.

In order to obtain a chart of the form of Fig. 81 it is necessary to calculate the molal volume corresponding to each observed value of pV and p . If pV is equal to 1.0 at standard conditions, V is termed the

relative volume, the ratio of the volume of any weight of gas under the existing conditions to the volume of the same weight of gas at standard conditions. To obtain the molal volume v , the corresponding relative volume V is divided by n the number of mols of gas occupying unit volume at standard conditions.

Thus

$$n = \frac{p_s \cdot 1.0}{p}$$

$$v = \left(\frac{pV}{p} \right) \frac{1}{n} = \left(\frac{pV}{p} \right) \frac{C_s RT}{p_s} \quad (20)$$

where C_s is the compressibility factor at standard conditions. In Fig. 81 compressibility factors are plotted against values of v calculated in this way.

The solid-line curves of Figs. 80 and 81 were plotted from the data of the International Critical Tables. The curves of Fig. 82 were derived from these. For the accurate use of such charts it is necessary that more isothermal curves shall be available than ordinarily are presented in the experimental data. Such intermediate curves may be established by graphical interpolation.

Experimental compressibility measurements are also frequently expressed in the form of *isometric* data showing the variation of pressure with change in temperature of a known weight of gas confined in a constant volume. Such isometrics are determined at various selected volumes. These data yield curves of the type of Fig. 82 directly. Curves of the types of Figs. 80 and 81 may then be derived by interpolation methods similar to those described above. A simpler method in this case is to reverse the method of plotting of Fig. 80 and plot curves relating compressibility factors to temperature, each curve corresponding to a constant molal volume.

Compressibility Factors from Reduced Temperature and Pressure. *Reduced temperature* is the ratio of the temperature at which a substance exists to its critical temperature, both being expressed in absolute units. Similarly, *reduced pressure* is the ratio of the existing to the critical pressure in absolute units.

When different gases are examined at like values of reduced temperature and reduced pressure it will be found that their compressibilities are nearly alike. Under such conditions of equal reduced pressure and reduced temperature, substances are said to be in corresponding states

where p_r = reduced pressure = p/p_c or $p = p_c p_r$
 T_r = reduced temperature = T/T_c or $T = T_c T_r$
 v_r = reduced volume = v/v_c or $v = v_c v_r$

By substituting these values of p , v and T into van der Waals' equation (1) and the values of p_c , v_c and T_c obtained from Equations (8), (7) and (9) a so-called *reduced equation of state* is obtained which is the same for all van der Waals' gases; that is,

$$w_r - 1 = 8T_r \quad (21)$$

At the critical state, by substituting the critical values into Equation (1) and the values of a and b obtained from Equations (5) and (7), van der Waals' equation reduces to

$$RT_c \quad (22)$$

that is, for a van der Waals' gas the critical volume is $\frac{3}{8}$ the volume of an ideal gas. This value has been found to apply to monatomic gases. For diatomic gases the ratio is 0.263, and for hydrocarbons of more than three carbon atoms the ratio is 0.26.

Although an exact equation of state is different for each gas a reduced equation of state is possible which applies approximately to all gases. Similarly the compressibility factors of all gases are nearly equal at corresponding states.

In Fig. 83 are plotted values of compressibility factor as a function of reduced temperature and reduced pressure. This chart was derived as an average of data reported in the literature for carbon dioxide, nitrogen, hydrogen, ammonia, methane, propane, and pentane and is not in entirely rigorous agreement with all the data on any one of these substances. However, these discrepancies, resulting from the fact that the theory of corresponding reduced states is only an approximation, are small enough that for many purposes the chart may be taken as applicable to any pure compound. It then constitutes a very convenient method for handling PVT calculations wherever the critical temperature and pressure are known. From this figure it will be seen that for all values of T_r less than about 2.5 the compressibility factor is less than 1.0 for values of p_r below 10. In this region actual gases are more compressible than the ideal. At values of p_r above 10 the compressibility factors of all gases exceed 1.

Figure 83 is a modification prepared by Watson and Smith¹ of a similar chart presented by Dodge² in an excellent résumé of high-pressure calculations. It was pointed out by Newton³ that in applying relationships of this type for hydrogen and helium better agreement is obtained by

¹ K. M. Watson and R. L. Smith, National Petroleum News, July, 1936.

² B. F. Dodge, Ind. Eng. Chem. **24**, 1353 (1933).

³ R. H. Newton, Ind. Eng. Chem. **27**, 302 (1935).

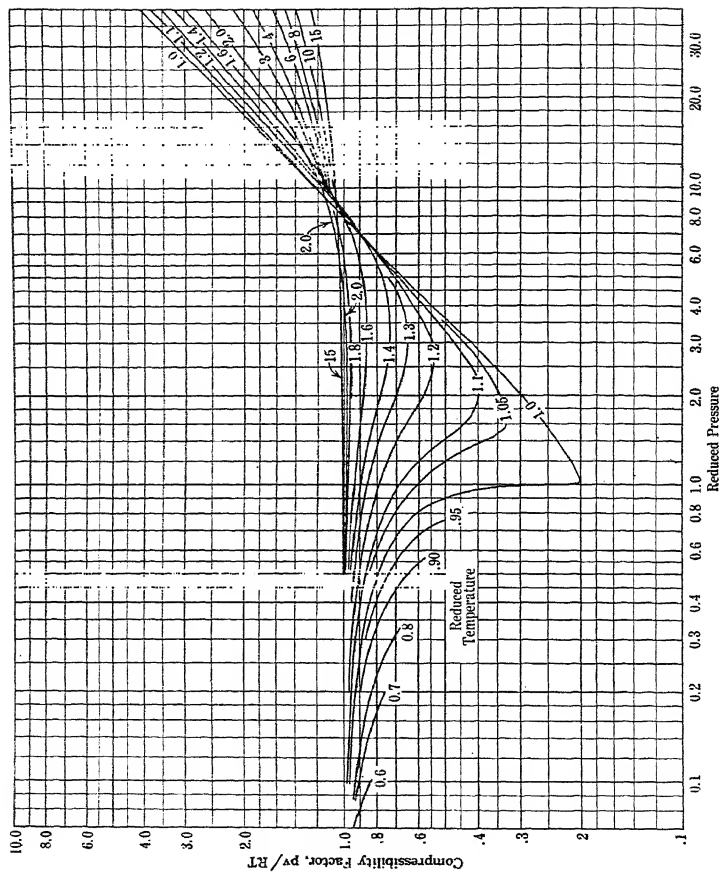


Fig. 83. Compressibility Factors of Gases and Vapors.

using modified reduced conditions calculated from the equations:

$$T_r = T/(T_c + 8); \quad p_r =$$

In calculations involving the conditions of gases at high pressure, Fig. 83 is employed in combination with the equation $pV = nCRT$. Values of V/n may be obtained directly when values of p and T are known. This represents the usual case. If either temperature or pressure is unknown the procedure requires modifications. These three cases are illustrated in the following problems.

Illustration 7. Volume Unknown. Calculate the volume occupied by 1 lb of methane at a temperature of 40° F and a gauge pressure of 1000 lb per sq in.

From Table XIX, page 383, the critical temperature of methane is -82.5° C or -116.5° F and the critical pressure 45.8 atmospheres or 673 lb per sq in.

$$\begin{aligned} \text{Reduced temperature} &= \frac{40 + 460}{-116.5 + 460} = 1.40 \\ \text{Reduced pressure} &= \frac{(1000 + 14.7)}{673} = 1.51 \\ \text{Compressibility factor (Fig. 83)} &= 0.84 \\ \text{Molecular weight} &= 16 \end{aligned}$$

$$R = \left[\frac{(\text{lb})}{(\text{in.})^2} \frac{(\text{ft})^3}{(\text{lb-mol})^\circ \text{R}} \right]$$

hence $\frac{nCRT}{p} = \frac{1(0.84)(10.71)(500)}{(16)(1014.7)} = 0.278 \text{ cu ft}$

Illustration 8. Pressure Unknown. Calculate the pressure necessary to compress 100 liters of nitrogen at a pressure of 745 mm Hg and 23° C to occupy a volume of 1.0 liter at -110° C.

$$\begin{aligned} p_c &= 33.5 \text{ atm} \\ T_c &= 126^\circ \text{ K} \\ \text{Initial } p_r &= \frac{0.982}{33.5} = 0.0293 \\ \text{Initial } T_r &= \frac{296}{126} = 2.35 \\ \text{Initial } C \text{ (from chart)} &= 1.00 \\ \text{Final } T_r &= \frac{163}{126} = 1.29 \\ \text{Final } p_r &= \frac{p_2}{33.5} \end{aligned}$$

From equation (18)

$$\frac{p_1 V_1}{p_2 V_2} = \frac{C_1 T_1}{C_2 T_2}$$

Substituting the known values

$$(0.982)(100) \quad 1.00 \quad \frac{296}{163}$$

$$C_2 = 0.0185 p_2$$

$$C_2 = (0.0185)(33.5) p_r = 0.621 p_r$$

The straight line corresponding to the equation $C_2 = 0.621 p_r$ is extended across the compressibility chart, Fig. 83. Since Fig. 83 is plotted on double logarithmic

scales this line must have a positive slope of 45° and pass through the point $C = 0.621$ where $p_r = 1.0$. The problem may be readily solved with the aid of a 45° triangle. Thus, where this line intersects the line $T_r = 1.29$ the value of C_2 will be found to be 0.80 and the value of $p_r = 1.30$.

Hence $p = (1.30) (33.5) = 43.6 \text{ atm}$

Illustration 9. Temperature Unknown. The volume occupied by 1 lb of *n*-octane at 27 atmospheres is 0.20 cu ft. Calculate the temperature.

$$t_c = 565^\circ \text{ F } (1025^\circ \text{ R})$$

$$p_c = 24.6 \text{ atm}$$

$$p_r = \frac{27}{24.6} = 1.10$$

$$T_r = \frac{T}{1025}$$

From Equation (17)

$$(27) (0.20) = \frac{114}{\frac{845}{T} - \frac{845}{1025 T_r}} = \frac{0.825}{T_r}$$

or

To solve problem graphically, C is plotted in Fig. 84 against T_r for a value of $p_r = 1.10$ from Fig. 83. On the same scales is plotted the equation values of $C = \frac{0.825}{T_r}$.

Where these two curves intersect, $C = 0.72$ and $T_r = 1.15$

Hence $T = 1025 T_r = (1025) (1.15) = 1180^\circ \text{ R}$ or 720° F .

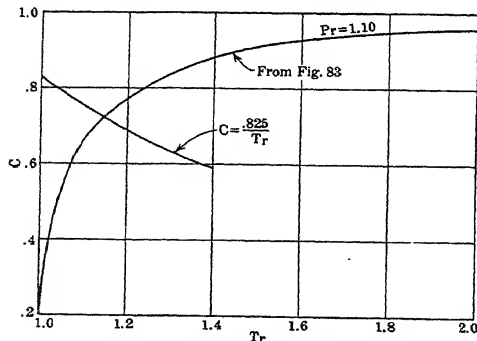


FIG. 84. Graphical Solution for T_r .

GASEOUS MIXTURES AT HIGH PRESSURES

The laws of additive pressures and of additive volumes discussed in Chapter III, page 47, when considered separately, do not necessarily imply ideal gases; indeed, for actual gases these laws apply with much

greater accuracy than the ideal gas law. Either Dalton's or Amagat's law may hold for actual gases, but together they hold rigidly only for ideal gases. Which of these laws gives the better approximation depends upon the conditions and the nature of the gaseous mixture. For mixtures of argon and ethylene Dalton's law of additive pressures is the more nearly accurate; for mixtures of nitrogen and hydrogen the law of additive volumes holds better.

Application of van der Waals' Equation to Mixtures. From van der Waals' equation,

$$p_A = \frac{RT}{V - n_A b_A} - \frac{a_A}{V^2}$$

where

V = total volume of mixture

n_A = number of mols of A in the mixture

a_A, b_A = van der Waals' constants of component A

p_A = partial pressure of A

Similar equations would represent the partial pressures of components B, C , etc. Combining these equations with Dalton's law:

$$\left[\frac{n}{V - n_A b_A} + \frac{n}{V - n_B b_B} + \frac{n_C}{V - n_C b_C} + \dots \right] - \frac{1}{V^2} [a_A n_A^2 + a_B n_B^2 + \dots] = p \quad (24)$$

Equation (24) expresses the relationship between the pressure, temperature, and volume of a gaseous mixture of specified composition. It may be solved without great difficulty for either p , T , or V . Since it is derived from a combination of Dalton's law and the van der Waals equation, it is subject to the limitations and errors of each.

The following illustration from the data of Masson and Dolley¹ shows the application of van der Waals' equation to gaseous mixtures in a special case.

Illustration 10. Calculate the pressure exerted by a mixture of 3.70×10^{-5} gram-mol of ethylene and 0.407×10^{-5} gram-mol of argon in a volume of 0.00419 cc at a temperature of 25° C.

Solution: First the pressure is calculated which would be exerted by each gas if present alone. The equation of van der Waals is used for this calculation.

$$\begin{array}{lll} \text{For ethylene:} & a = 4.48 \times 10^6 & b = 57.2 \\ & V = 4.19 \times 10^{-3} & n = 3.70 \times 10^{-5} \end{array}$$

$$\begin{aligned} p &= \frac{RT}{V - nb} - \frac{a}{V^2} \\ &= \frac{3.70 \times 10^{-5} \times 82.1 \times 298}{0.00419 - (57.2 \times 3.70 \times 10^{-5})} - \frac{4.48 \times 10^6 \times 13.65 \times 10^{-10}}{17.6 \times 10^{-6}} \\ &= 438 - 348 = 90 \text{ atmospheres, the pressure of the ethylene if present alone.} \end{aligned}$$

¹ Masson and Dolley, Proc. Royal Soc. 103A, 524 (1923).

In a similar manner, the pressure which would be exerted by the argon alone may be calculated and found to be 23.6 atmospheres. Then, the total pressure of the mixture is $90 + 23.6 = 113.6$ atmospheres.

The actual measured pressure of the mixture was found to be 100.4 atmospheres. The overall error in the use of van der Waals' equation combined with Dalton's law is +13 per cent. The error introduced by Dalton's law is +3 per cent. The error due to the use of van der Waals' equation is therefore +10 per cent, which results from the fact that the specified conditions of temperature and pressure are very close to the critical state, the most unfavorable region for the use of van der Waals' equation.

If the gases were assumed to obey the ideal gas law the calculated pressure would be 240 atmospheres, an error of 140 per cent. It is therefore apparent that the combination of van der Waals' and Dalton's laws, though by no means rigorously correct, offers a great improvement over the ideal gas law. The above illustration represents an extreme case with unusually large errors because of the fact that the ethylene was very close to its critical state.

The application of Amagat's law in conjunction with the van der Waals equation is complicated in that it involves solving for partial volumes for each component gas and then adding these to find the total volume. Applying the van der Waals equation to component *A*, there results

(25)

Similar equations may be obtained for components, *B*, *C*, etc. The partial volumes must be solved separately by trial or graphical methods.

Mean Compressibility Factors. A simple empirical equation or state for a mixture of gases may be written in a form similar to Equation (17).

$$pV = C_m n_i RT \quad (26)$$

where

- p = total pressure of mixture
- V = total volume of mixture
- C_m = mean compressibility factor of mixture
- n_i = total number of mols of gases in mixture

Equation (26) permits calculation of the pressure, temperature, and volume relationships of gaseous mixtures of known compositions if the mean compressibility factors are known. The mean compressibility factor is a function of the pressure, temperature, and composition of the mixture. By exactly the same methods which were described for a pure gas, the compressibility factors of a mixture of fixed composition may be determined and expressed graphically as a function of pressure, temperature,

or molal volume. In order to obtain complete information regarding a particular system these measurements must be repeated with mixtures of different compositions. Because of the tremendous amount of experimental work involved, only a few simple systems of binary gaseous mixtures have been investigated and only over relatively narrow ranges of conditions. In the International Critical Tables¹ are references to the original literature from which such information may be obtained.

E. P. Bartlett² has carried out a series of careful determinations for mixtures of hydrogen and nitrogen at a temperature of 0° C. The results of this investigation are shown graphically in Figs. 85 and 8.6

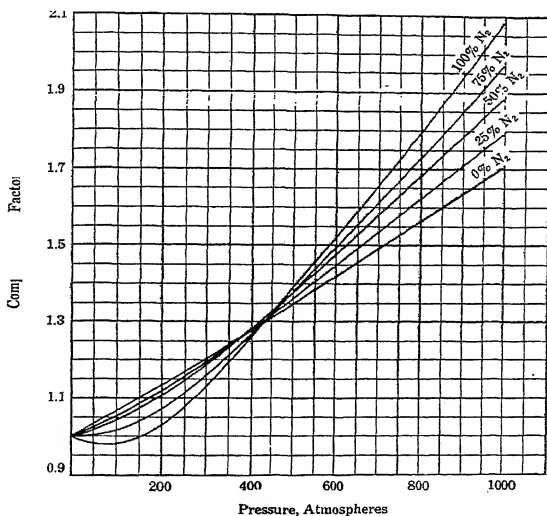


FIG. 85. Compressibility Factors of Mixtures of Hydrogen and Nitrogen at a Temperature of 0° C.

In Fig. 85 is shown the variation of the mean compressibility factor with pressure for mixtures of various molal compositions. In Fig. 86 is shown the variation of the compressibility factor with the composition of the mixture at various pressures. If Amagat's law is assumed to

¹ Vol. III, p. 17.

² J. Am. Chem. Soc. **49**, 687-701, 1955-1958 (1927).

apply, an expression for the mean compressibility factor follows:

$$n_i \quad (27)$$

where

C_A = compressibility factor of component A at the temperature and total pressure of the mixture.

This equation permits the approximate calculation of the mean compressibility factor of a mixture, at any conditions of temperature and

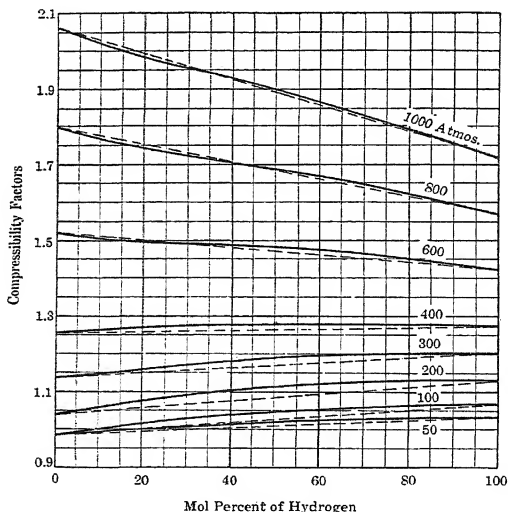


FIG. 86. Compressibility Factors of Mixtures of Hydrogen and Nitrogen at a Temperature of 0° C.

pressure, from the compressibility factors of the component gases at the same conditions. The dotted lines on Fig. 86 represent the results obtained by the application of Equation (27) to the mixtures of hydrogen and nitrogen at the conditions investigated. It will be noted that, for this system, the validity of Amagat's law is satisfactory, the maximum error being of the order of 2.5 per cent.

Compressibility Factors for Gaseous Mixtures from Corresponding States. Where the critical temperature and critical pressure of the component gases in a mixture are known it is convenient to calculate

mean compressibility factors from Equation (27), obtaining the compressibility factor of each component gas from Fig. 83, at the total pressure of the mixture. This simplified method is based upon the validity of Amagat's law of additive volumes. The procedure avoids the use of all equations of state and the necessity of constructing compressibility-factor charts for each different system.

The use of compressibility factors of component gases in conjunction with Amagat's law is satisfactory for calculating the compressibility of many mixed gases. Large errors appear to result only when the conditions of the mixture are close to the critical points of some of the important components.

Illustration 11. A gas containing 6 lb of methane and 4 lb of ethylene is compressed to 80 atmospheres at 50° F. Calculate the volume occupied by the compressed gas.

$$\text{Pound-mols of methane} = \frac{6}{16.04} = 0.374$$

$$\text{Pound-mols of ethylene} = \frac{4}{28.04} = 0.143$$

$$\text{Total pound-mols} = 0.517$$

$$\text{Mol fraction of methane} = 0.724$$

$$\text{Mol fraction of ethylene} = 0.276$$

$$\text{Critical temperature of methane} = -82.5^{\circ} \text{C or } 343^{\circ} \text{R}$$

$$\text{Critical temperature of ethylene} = 9.7^{\circ} \text{C or } 510^{\circ} \text{R}$$

$$\text{Critical pressure of methane} = 45.8 \text{ atm}$$

$$\text{Critical pressure of ethylene} = 50.9 \text{ atm}$$

$$\text{Reduced temperature of methane} = \frac{510}{343} = 1.49$$

$$\text{Reduced temperature of ethylene} = \frac{510}{510} = 1.0$$

$$\text{Reduced pressure of methane} = \frac{80}{45.8} = 1.75$$

$$\text{Reduced pressure of ethylene} = \frac{80}{50.9} = 1.57$$

Mean compressibility factor of mixture

$$C_m = (0.724)(0.86) + (0.276)(0.25) = 0.69$$

$$V = \frac{n C_m R T}{p} = \frac{(0.517)(0.69)(0.729)(510)}{80} =$$

A comparison of the results obtained by calculating the volume of a gaseous mixture by various methods described in this chapter are tabulated herewith. The mixture consists of 1 gram of 45 mol per cent hydrogen and 55 mol per cent nitrogen at a temperature of 0° C and pressure of 350 atmospheres. The experimental value was found to be 4.77 cubic centimeters.

	Total Volume cc	Partial Volume		Partial Pressures	
		Hydrogen	Nitrogen	Hydrogen	Nitrogen
a. By assuming ideal gas law.....	3.92	1.76	2.16	157.5	192.5
b. van der Waals' equation with Dalton's law....	4.11	2.33	2.61	171	179
c. van der Waals' equation with Amagat's law....	4.94	2.33	2.61	139	146
d. Compressibility factor for pure gases, Fig. 85 and Dalton's law.....	4.16	2.20	2.57	164	186
e. Compressibility factor for pure gases, Fig. 85 and Amagat's law.....	4.77	2.20	2.57	142	158
f. Compressibility factors, Fig. 83 and Dalton's law.....	4.16	2.17	2.59	163	187
g. Compressibility factor, Fig. 83 and Amagat's law.....	4.76	2.17	2.59	141	162

From the above chart it is evident that for mixtures of nitrogen and hydrogen Amagat's law of additive volumes holds almost exactly but Dalton's law of additive pressure is greatly in error.

Critical Phenomena of Mixtures. The behavior of a mixture in the region of the critical point is best understood by reference to Fig. 86a, in which pressure is plotted against temperature, both on uniform scales.

Curve *AC* represents the vapor-pressure curve of a pure compound having the critical temperature and pressure corresponding to point *C*. For a single-component system the area to the left of this curve represents the region of the liquid phase, and the area below it is region of the vapor phase.

The sloping straight lines on Fig. 86a are lines of constant volume for the single-component system. These lines are termed *isochors* or *isometrics*. It has been found that for most substances the isometrics are approximately straight, represented by the equation,

$$p - b \quad (28)$$

where *m* and *b* are constants dependent on the volume and the substance under consideration.

Curve *BDEC'FGH* represents what is termed the *border curve* of a mixture having the same average volatility as that of the pure compound represented by line *AC*, but made up of two or more substances of different volatilities. The area enclosed by the border curve represents a two-phase region in which both liquid and vapor are present in equi-

librium. Line BDE represents conditions of initial vaporization, to the left of which is the region of complete liquefaction. Line HGF represents conditions of initial condensation below which is a region of complete vaporization. This line is termed the dew-point curve of the mixture. Line BDE is termed the *bubble-point curve*.

Point C' represents the critical point of the mixture at which there is continuity of phases. In general the critical temperature of a mixture is somewhat higher and the critical pressure considerably higher than those of a pure compound having the same average volatility.

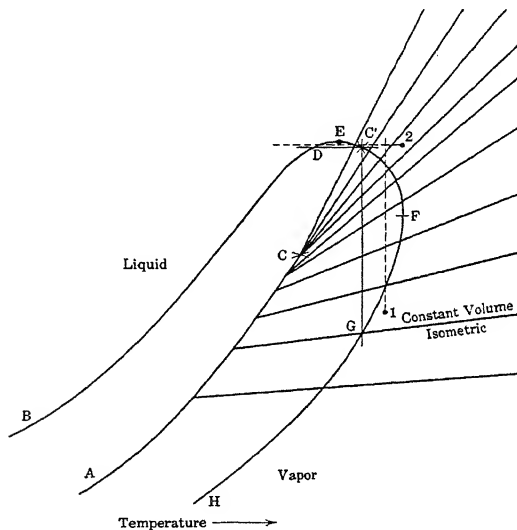


FIG. 86a. Comparison of PVT and Vaporization Diagrams of Mixture and Pure Compound.

It will be noted that the dew-point curve passes through a maximum temperature at F . Thus, in the case of a mixture, liquid may exist at a temperature higher than the critical. The maximum temperature F on the border curve is termed the *critical condensation temperature* or *cricondentherm*. Similarly, in the case of many mixtures the initial vaporization curve passes through a point of maximum pressure, E .

The areas GFC' and DEC' represent regions of *retrograde condensation*. Thus, if the mixture at the conditions of point 1 is compressed

at constant temperature, a more dense second phase appears when line GF is reached. As the pressure is increased, the quantity of this more dense phase increases to a maximum and then diminishes, disappearing entirely when line FC' is reached. Similarly, if the mixture at conditions of point 2 is cooled at constant pressure, a less dense phase appears when line $C'E$ is reached which increases to a maximum quantity as cooling is continued and then diminishes and disappears as line DE is reached.

The entire area outside the border curve is a region of homogeneous fluid in which no phase separations occur.

Pseudo Critical Point. It was shown by Kay¹ that the PVT data of a gaseous mixture may be satisfactorily correlated by the generalized compressibility factor curves of Fig. 83 if the proper values of *pseudo critical* temperature and pressure are used for the calculation of reduced temperatures and pressures. For all except pure compounds, or mixtures of compounds differing little in physical properties, the pseudo critical temperature and pressure are less than the true critical temperature and pressure.

It was found that the pseudo critical point is satisfactorily determined as the molal average of the critical properties of the components. Thus, the pseudo critical temperature of a mixture is the molal average of the critical temperatures of the components, and the pseudo critical pressure is the molal average of the component critical pressures. As pointed out above, the true critical point of the mixture cannot be obtained in this manner and is at a higher temperature and pressure.

Referring to Fig. 86a, the mixture having a true critical point C' has a pseudo critical point C which is the true critical point of what may be termed the *equivalent pure compound* of the same average molecular weight and volatility. The isometrics of the mixture will then coincide with those of the equivalent pure compound at conditions outside the border curve defining the two-phase region.

Once the pseudo critical point is established, PVT calculations on a mixture are carried out exactly as for a pure compound, using the average molecular weight of the mixture. Compressibility factors are determined from Fig. 83, using the pseudo reduced temperature and pressure. However, it must be emphasized that this method applies only to the single-phase region and may break down entirely at conditions within the border curve of the mixture. The pseudo critical point itself is located in this region.

¹ "The Density of Hydrocarbon Gases and Vapors at High Temperatures and Pressures," by W. B. Kay, presented at the meeting of the American Chemical Society, Kansas City, Missouri, April 15, 1936.

Illustration 12. Calculate the volume occupied by 1 lb of a mixture of 59.9 mol per cent ethylene and 40.1 per cent argon at a temperature of 25° C and a pressure of 100 atmospheres.

	Ethylene	Argon
Critical temperature, °C	9.7	-122
Critical pressure, atmospheres	50.9	48
Molecular weight	28	39.9

$$\text{Pseudo critical temperature} = (0.599 \times 283) + (0.401 \times 151) = 230^\circ \text{ K}$$

$$\text{Pseudo critical pressure} = (0.599 \times 50.9) + (0.401 \times 48) = 49.7 \text{ atm}$$

$$\text{Average mol weight} = (0.599 \times 28 + 0.401 \times 39.9) = 32.7$$

$$\text{Pseudo reduced temperature} = 298/230 = \dots\dots\dots 1.3$$

$$\text{Pseudo reduced pressure} = 100/49.7 = \dots\dots\dots 2.01$$

$$\text{Compressibility factor (Fig. 83)} = \dots\dots\dots 0.70$$

$$\text{Volume} = \frac{359 \times 0.70}{32.7} \times \frac{298}{273} \times \frac{1}{100} = \dots\dots\dots 0.084 \text{ cu ft}$$

The experimental measurements of Masson and Dolley indicated a compressibility factor of 0.712 as compared to the value of 0.70 derived from Fig. 83 and the pseudo critical point in the above illustration.

It is believed that use of the pseudo critical point together with reduced compressibility factors is the most satisfactory and convenient generalized method for handling PVT calculations on gaseous mixtures, particularly at conditions near the critical. In this region it is more reliable than either Dalton's or Amagat's laws.

Additivity of Intrinsic Pressures. A principle termed the *additivity of intrinsic pressures* was developed by Gilliland¹ as a substitute for Dalton's and Amagat's laws which assume additivity of partial pressures and partial volumes respectively. In brief, this method postulates that the PVT data of a mixture may be represented by isometrics as shown in Fig. 86a, which at least over certain ranges are straight lines represented by the equation

$$p_{\text{mix}} = m_{\text{mix}}T - b_{\text{mix}} \quad (29)$$

The equation of an isometric of the mixture is obtained by averaging the constants of the equations of the same isometric of each component gas. It was found that the following equations gave average isometrics in best agreement with experimental data.

$$x_1 + x_2 m_3 + \dots \quad (30)$$

$$\frac{1}{2}^2 + \dots \quad (31)$$

where x = mol fraction

m = slope of the isometric curve corresponding to a molal volume v for both the mixture and each component

b = intercepts of the isometric curves of the mixture and components, where $T = 0$

Equations (29) and (30) may be combined to give

$$p_{\text{mix}} + b_{\text{mix}} = x_1 (p_1 + b_1) + x_2 (p_2 + b_2) + \dots \quad (32)$$

¹ E. R. Gilliland, Ind. and Eng. Chem. 28, 212-15 (1936).

For binary mixtures (31) and (32) may be combined with the equation $x_1 = 1 - x_2$ to give,

$$x_1 p_1 + x_2 p_2 + x_1 x_2 (\sqrt{b_1} - \sqrt{b_2})^2 \quad (33)$$

Equations (30) and (31) or (33) may be used for calculating the equation of any isometric curve if the equations of the isometric curves of the same molal volume are known for each component.

Application of this method to the existing data on mixtures indicates it to be of a much higher order of accuracy than Dalton's or Amagat's laws. It is believed to be the most reliable method available for estimating properties of mixtures from complete data on the components. However, it is relatively cumbersome to use, and where calculations are made from generalized compressibility factor curves, the pseudo critical point method described above is much more convenient and probably as accurate as the generalized data on the components warrant.

PROBLEMS

1. For the production of liquid oxygen it is desired that the gas be compressed to a pressure of 100 atmospheres at a temperature of -90°C . Oxygen at a pressure of 14.5 lb per sq in. and a temperature of 22°C is compressed to these conditions; Calculate the volume of compressed gas resulting from 100 cu ft of the original: (a) from van der Waals' equation; (b) from compressibility factors (Fig. 83).
2. In one cylinder of a multistage compressor, carbon dioxide is compressed from a volume of 2 cu ft at a pressure of 14.6 lb per sq in. and a temperature of 22°C , to a volume of 0.4 cu ft at a temperature of 30°C . Calculate the pressure necessary: (a) using the van der Waals equation; (b) from Fig. 83.
3. Calculate the volume occupied by 10 lb of chlorine when compressed to a pressure of 125 lb per sq in. at a temperature of 30°C : (a) using the van der Waals equation; (b) from Fig. 83.
4. Methyl chloride for use in domestic refrigerators is sold in small cylinders having volumes of 0.15 cu ft. Calculate the weight of methyl chloride gas contained in a cylinder if the absolute pressure is 68 lb per sq in. and the temperature 20°C : (a) using the van der Waals equation; (b) from Fig. 83.
5. For high-pressure distribution in long pipe lines it is proposed to compress natural gas (methane) to an absolute pressure of 500 lb per sq in. Calculate its density in pounds per cubic foot at this pressure and a temperature of 80°F : (a) using the van der Waals equation; (b) from Fig. 83.
6. Sulphur dioxide is compressed from a pressure of 14.6 lb per sq in. and a temperature of 75°F to a pressure of 65 lb per sq in. at a temperature of 88°F . Calculate the ratio of the initial to the final volume: (a) using van der Waals' equation; (b) from Fig. 83.
7. In order to study the effect of steam on steel at high temperatures and pressures, a short length of pipe is capped on both ends and heated after a certain amount of water has been placed in it. In filling the pipe, air is excluded by first heating it to 212°F and passing dry steam through it at a pressure of 14.7 lb per sq in. Liquid water is then added and the pipe quickly capped. It is desired that the steam in the pipe shall exert a pressure of 500 lb per sq in. when heated to a temperature of 600°F . Calculate the weight of water which should be added to the steam-filled pipe if its volume is 20 cu in. The volume of the water may be neglected as compared with that of the steam. It may be assumed that dry steam at atmos-

pheric pressure obeys the simple gas law, but where higher pressures are involved the van der Waals equation should be used. Neglect expansion of steel.

8. Using the data of Figs. 80, 81, and 82, calculate the density in pounds per cubic foot of nitrogen at a pressure of 900 lb per sq in. and a temperature of -40°C .

9. Using the data of Figs. 80, 81, and 82, calculate the pressure necessary to compress 100 liters of nitrogen at a pressure of 745 mm. of Hg and 23°C , to occupy a volume of 2.0 liters at a temperature of 40°C .

10. Using the data of Figs. 80, 81, and 82, calculate the temperature to which 1.2 lb of nitrogen must be cooled in order that it may exert a pressure of 50 atmospheres when confined in a volume of 0.27 cu ft.

11. From the data of the International Critical Tables, calculate the compressibility factors of ethylene at a temperature of 20°C and at pressures ranging from 0 to 500 atmospheres. Plot these compressibility factors against pressure in atmospheres and also against molal volumes in cubic centimeters per gram-mol.

12. From the data of problem 11, calculate the volume occupied by 50 grams of ethylene at a temperature of 20°C and a pressure of 5000 lb per sq in.

13. Using the Beattie-Bridgman equation, calculate the pressure exerted by 30 liters of air, measured at 20°C under a pressure of 740 mm of Hg, when compressed into a volume of 200 cc at a temperature of 0°C . It may be assumed that at the lower pressure the simple gas law is applicable.

14. For ethylene gas the value of pV at 20°C and 100 atmospheres is 0.3600 referred to a value of unity at 0°C and 1 atmosphere. The density of ethylene gas at standard conditions is 1.2604 grams per liter. Calculate the volume of 1 gram-mol at 20°C and 100 atmospheres.

15. Calculate the volume occupied by 1 gram-mol of carbon dioxide gas at its critical state when the product $pV = 0.6379$ referred to 1.00 at 0°C and 1 atmosphere.

16. A mixture of hydrogen and nitrogen contains 45 mol per cent of hydrogen. Calculate the volume in cubic centimeters occupied by 1.0 gram of this mixture at a pressure of 350 atmospheres and a temperature of 0°C .

a. Assuming the ideal gas law.

b. Using van der Waals' equation and Dalton's law.

c. Using van der Waals' equation and Amagat's law.

d. Using compressibility factor of the component gases given in Fig. 85 with Dalton's law.

e. Using compressibility factor of the component gases given in Fig. 85 with Amagat's law.

f. Using compressibility factors from reduced states (Fig. 83) with Dalton's law.

g. Using compressibility factors from reduced states (Fig. 83) with Amagat's law.

The experimental volume was found to be 4.77 cc.

17. Calculate the partial volumes and partial pressures of the hydrogen and of the nitrogen under the conditions of Problem 16 for each of the methods designated.

18. A mixture of 60 mol per cent methane and 40 per cent propane exists at a temperature of 55°C and a pressure of 80 atmospheres.

(a) Calculate the pseudo critical temperature and pressure of the mixture and its density in grams per liter by the pseudo critical method. Compare this result with the experimental value of Sage, Lacey and Schaafsma, *Ind. Eng. Chem.* **26**, 215 (1934).

- (b) Calculate the density assuming Dalton's law and Fig. 83.
(c) Calculate the density assuming Amagat's law and Fig. 83.

The critical properties of methane and propane are as follows:

	Methane	Propane
Critical temperature, degrees C	-82.5	95.6
Critical pressure, atmospheres	45.8	43

CHAPTER XII

ENTROPY AND FREE ENERGY

For the treatment of problems involving equilibria and thermal properties at high pressures the thermodynamic concepts of entropy and free energy are indispensable. These concepts are introduced in an elementary manner at this point and are developed sufficiently to form a basis for the derivation of thermodynamic equations of practical applicability in the calculations of equilibria and high pressure behavior. For a more extensive treatment reference should be made to the text of Lewis and Randall¹ from which many of the concepts herein presented were taken.

Applications of the principles here developed are demonstrated in following chapters.

Reversibility and Irreversibility. In thermodynamic terms a *system* refers to a substance or group of substances under consideration and a *process* to the changes taking place in the properties of the system. Thus, hydrogen, oxygen, and water may constitute a system, and the combustion of the hydrogen to form water, the process.

It is a natural phenomenon that any system left to itself without external influence will tend to change toward a state of rest or equilibrium. Changes which occur within a system entirely unaided by external agencies are said to be *spontaneous* and can proceed only in the direction of a state of rest.

A *reversible process* is defined as one proceeding under conditions of balanced forces in which the direction of change of the process may be reversed at any stage by an infinitesimal change in external conditions. An example of a reversible process is the vaporization of a liquid under its own vapor pressure in a cylinder fitted with a frictionless piston. At any stage an infinitesimal increase in pressure will produce condensation, and an infinitesimal decrease will cause vaporization. On the contrary, the flow of heat from a hot to a colder body is an irreversible process, the direction of which can be changed only by finite changes produced by an external agency. Similarly, the flow of a liquid from a high to a lower level is irreversible.

The *first law of thermodynamics* states that energy cannot be created or destroyed and that in any isolated system the total energy content

¹ "Thermodynamics," Lewis and Randall, McGraw-Hill, 1923.

remains unchanged for any process. However, in an irreversible process it is evident that the *availability* of energy, or its ability to do work in changing to a lower form, is reduced. When a given quantity of heat passes from one body to another the heat transferred cannot be restored to the original body except from a third body at a still higher temperature or by the conversion of other forms of energy taken from an external source. On the contrary, in a reversible process, an infinitesimal change will tend to restore the original condition, no degradation of energy takes place in the system as a whole, and the availability of its energy content remains constant.

Another example of an irreversible process and the degradation of the energy of a system is in the free expansion of a gas. If a gas is confined in a closed container of space v_1 and allowed to expand into a vacuum chamber such that the new total volume is v_2 , and if this system is entirely isolated by rigid walls from its surroundings, the gas is said to *expand freely*. No work is performed upon the surroundings, and for an ideal gas there is no change in temperature. The energy content of the expanded gas is the same as of the original gas. However, in order to return the expanded gas to its original condition the expenditure of external energy will be required. Work of compression must be done upon the gas. This work will manifest itself as heat in compressing the gas and for isothermal compression in turn be given up by the system and be transferred to the surroundings. In isothermal compression of an ideal gas the energy content remains constant but assumes a higher level of availability. The expansion of a gas represents a degradation process.

Similarly, if two different ideal gases, both at the same temperature and pressure, are allowed to diffuse one into the other this process will be accompanied by no change in energy, and yet to restore the system to its original state will require the expenditure of energy from an outside source. Mixed gases represent a lower state of degradation than the original unmixed gases.

ENTROPY

The property termed *entropy* is employed to represent the degradation of a system or the unavailability of its energy. In the examples of the preceding section the expanded gas has a higher entropy than the same gas at high pressure and at the same temperature, and the mixed gases have a higher entropy than the total of the separate gases at the same temperature and pressure.

One statement of the *second law of thermodynamics* is that all naturally occurring and spontaneous processes are to some extent irreversible and accompanied by degradation of the system and an increase in entropy.

In an ideal reversible process or in a system in equilibrium, the entropy of the entire system must be constant, although various parts of it may undergo compensating increases or decreases in entropy. This follows from the requirement that in a reversible process an infinitesimal change in external conditions will restore the system to its initial state and hence there can be no degradation.

As an example, if a spinning flywheel is stopped by a brake the mechanical energy it possesses is converted into heat by friction. In general the conversion of any other form of energy into heat is an irreversible process, and hence must be accompanied by an increase in the entropy of the system. On the contrary, if this flywheel were stopped by a frictionless transmission that would use its energy to set another similar flywheel spinning, the process would be reversible and the system would undergo no change in entropy.

Since heat is the lowest form of energy, into which all other forms are spontaneously degraded, the entropy of a system is increased by the conversion of any other form of energy which it possesses into heat. Furthermore, heat can be added to an isolated system only through conversion of other forms of energy already possessed by it, into heat. Thus the magnitude of entropy increase in such a system is dependent upon the quantity of heat added to it in this manner.

However, the quantity of heat added is not the sole measure of entropy increase. Since heat is transferred irreversibly from a region of high to low temperature, it follows that addition of heat at a low temperature level is a more highly irreversible process than at a high temperature. Thus, the definition of entropy must be such that entropy is increased by conversion of other forms of energy into heat and also increased by a decrease in temperature level without the removal of heat. It must express both the quantity of energy degraded into heat and the temperature level to which it is degraded.

In order to formulate a quantitative definition of entropy, one more factor must be considered in addition to the amount of heat added to the system and the temperature level at which it is added. For example, an ideal gas may be freely expanded to a lower pressure within an isolated system. As previously pointed out, this is an irreversible process resulting in degradation of the system and an increase in entropy. However, no heat is added to the system and the process is isothermal. In this case the entropy increase is not measured by the addition of heat.

The same final result might be produced by expanding the gas through an engine within the system and converting the work done by the engine into heat by means of friction. In this case heat is added to the system by degradation of a higher form of energy. The amount of heat added

will increase as the efficiency of the engine is increased and will be a maximum if the engine operates reversibly.

In changing a system between given initial and final conditions the heat added may vary from zero to a maximum, depending upon the degree of irreversibility of the changes taking place. However, the change in entropy of the system must be constant and dependent only on initial and final conditions. Thus, the entropy increase of the system is measured by the heat added only when the changes taking place occur reversibly.

The three requirements discussed above are satisfied by the following mathematical definition of entropy. In any reversible process the increase in entropy of the system or of any part of the system is given by the following equation:

$$dS = \frac{dq}{T} \quad (1)$$

where

dS = increase in entropy S

dq = heat added

T = absolute temperature

This equation may be taken as a partial expression of the second law of thermodynamics.

It is evident that for the same process more heat will be transferred in a system of large mass than in a smaller one. Thus, like energy content or volume, entropy is an *extensive property* the magnitude of which is dependent upon the mass involved. In contradistinction, temperature and pressure are *intensive properties* independent of the quantity of material under consideration. As with energy contents, treatment of entropies can be made with relative values rather than with absolute numerical values. Tables of relative entropies may be established on the basis of a selected reference state just as is done in the case of internal energy and enthalpy.

An investigation by Nernst has indicated that at the absolute zero of temperature the entropy of any pure crystalline substance relative to its elements is zero. This principle is known as the *third law of thermodynamics* and forms the most desirable basis of experimentally determining values of entropy.

Calculation of Changes in Entropy. The changes in entropy taking place when a body receives heat at constant temperature and at constant pressure as in fusion, evaporation, and transition are obtained simply by dividing the increase in heat content by the absolute temperature. The increase in the entropy during vaporization per mol of liquid has already been referred to as Trouton's ratio in Chapter V.

Illustration 1. It is desired to calculate the entropy change in the fusion and in the vaporization of ethyl alcohol at atmospheric pressure.

Ethyl alcohol melts at 159° K with a heat of fusion of 1150 calories per gram-mol. Since fusion and vaporization are reversible isothermal processes, the molal entropy increase of fusion is equal to

$$\Delta S = \frac{\Delta q}{T} = \frac{1150}{159} = 7.24 \text{ cal per gram-mol} - ^\circ\text{C}$$

The heat of vaporization of ethyl alcohol at atmospheric pressure is 9400 calories per gram-mol at a normal boiling-point of 351° K. Hence the increase in entropy in vaporization is

$$\Delta S = \frac{\Delta q}{T} = \frac{9400}{351} = 25.7 \text{ cal per gram-mol} - ^\circ\text{C}$$

It will be observed that the units of entropy are the same as for heat capacity.

When heat is added with a resultant temperature rise the increase in entropy must be calculated by integration of Equation (1) over the required temperature range, thus

$$\frac{c_p}{T} \quad (2)$$

Illustration 2. Calculate the increase in entropy when 1 kg-mol of CO₂ gas is heated from 0° C to 1000° C at atmospheric pressure. The heat capacity of CO₂ expressed in terms of absolute temperature, °K is given on page 113 as

$$c_p = 7.713 + 0.00526T - 0.83 \times 10^{-6} T^2$$

$$\begin{aligned} \Delta S &= \int_{T_1}^{T_2} \frac{c_p}{T} dT = \int_{273}^{1273} \left(\frac{7.713}{T} + 0.00526 - 0.83 \times 10^{-6} T \right) dT \\ &= 16.50 \text{ Cal per kg-mol} - ^\circ\text{C} \end{aligned}$$

In calculating the entropy of a substance with reference to standard conditions it is necessary to add the entropy changes for each transition and for each temperature rise occurring exactly as was done in calculation of relative heat contents.

FREE ENERGY

A property which is more useful than entropy as a criterion of equilibrium is termed *free energy*, F , and is defined by the relation

$$F = H - TS \quad (3)$$

or for changes at constant temperature

$$\Delta F = \Delta H - T\Delta S \quad (4)$$

In a reversible process at constant temperature $T\Delta S = q$, and, from Equations (5) and (1), Chapter V,

$$\begin{aligned} \Delta F &= \Delta H - q = \Delta E + \Delta(pV) - \Delta E - w_e - w_f \\ \text{or} \quad \Delta F &= \Delta(pV) - w_e - w_f \end{aligned} \quad (5)$$

In any process at constant pressure, $\Delta(pV) = p\Delta V = w_e$. Then, in a reversible operation at constant pressure and temperature,

$$-\Delta F = w_f \quad (6)$$

where w_f = work in radiant or electrical forms done by the system.

In a reversible process at constant temperature and pressure there is no entropy change in the system as a whole and hence no degradation of energy. Therefore, the magnitude of the possible electrical and radiant work done by the system must be a maximum under these conditions. Thus, the decrease in free energy in an isothermal process at constant pressure is equal to the maximum possible value of w_f , the energy expended by the system in electrical or radiant forms which is realized only in a reversible operation. The term w_f is termed the *useful work* accompanying a process as distinguished from w_e , the *work of expansion*, and the sum $w_f + w_e$ which is termed the *total work*.

Since all actual processes are to some extent irreversible, it follows that the useful work which can be performed is less than the decrease in free energy, or $-\Delta F > w_f$. In processes so conducted that there are no external forces except a constant pressure, there is no opportunity for the performance of work by electrical or radiant means and $w_F = 0$. Common chemical reactions are of this type. It follows that such reactions cannot proceed unless accompanied by a decrease in free energy so that $-\Delta F > 0$.

Thus, the difference between the free energy of the products and the reactants of a reaction proceeding under at constant temperature and pressure with no other external forces determines whether or not it is possible for the reaction to occur spontaneously. If the change in free energy is positive the reaction is impossible. If it is negative the reaction is possible but may proceed at an immeasurably slow rate.

By analogy to the flow of electricity, the negative free energy change $-\Delta F$ is a driving force comparable to voltage. With a positive driving force a reaction may proceed at a rate determined by the retarding forces, just as under the influence of a voltage difference current will flow at a rate determined by the resistance of the circuit.

From Equation (4) it is evident that $-\Delta F$, the free energy change of a reaction, is equal to $-\Delta H$, the heat of reaction, only in the special case where $\Delta S = 0$. Actual values of $-\Delta F$ and $-\Delta H$ may be of different orders of magnitude or of different sign.

Equilibrium. A state of *equilibrium* is reached in a system when all forces and reactions are exactly balanced by other forces and reactions so that no net change is produced. In order that equilibrium may exist

it is necessary that every infinitesimal process taking place or tending to take place shall be reversible.

In the case of equilibrium in a chemically reacting system it is necessary that the temperature and pressure be uniform throughout the system. Non uniformities would be equalized by flow of heat or material. Therefore any reactions tending to take place at equilibrium conditions must be at constant temperature and pressure. In order that equilibrium be maintained it is necessary that no such process shall take place to change the conditions of the system. Thus, from the relationships of the preceding section, it becomes a necessary criterion of equilibrium that with respect to every possible process,

$$dF = 0 \quad (7)$$

The use of free energy as a criterion of equilibrium through Equation (7) is its most important application. From this equation it is possible to calculate, as demonstrated in Chapters XIII and XIV, the conditions existing when chemical reactions or physical changes proceed to equilibrium.

It must again be emphasized that free energy changes and differences indicate the tendency of a change to take place but give no indication as to the rate at which it will occur. The composition of a reacting system at equilibrium conditions may be calculated from the free energy changes involved, but no indication is given as to the time required to reach these conditions.

Maximum Total Work. As previously pointed out, the *total work* performed by a process includes the useful work produced plus the work done in expansion of the system and will be a maximum in a reversible process. In a reversible process at constant pressure

$$-\Delta A = -\Delta F + p\Delta V \quad (8)$$

or

$$\Delta A = \Delta F - p\Delta V \quad (9)$$

where

$$-\Delta A = \text{the maximum total work}$$

and

$$-\Delta F = \text{decrease in free energy} = \text{the maximum useful work.}$$

The function A bears the same relation to F as E does to H and may be defined as

$$A = E - TS \quad (10)$$

or at constant temperature

$$\Delta A = \Delta E - T\Delta S \quad (11)$$

There has been considerable confusion between the concepts of free energy F and maximum total work A . Although the differences are usually slight they are equal in a process at constant pressure only when there is no change in volume.

The concept of maximum total work A is useful for the derivation of certain thermodynamic relationships, but it is change in the free energy F which furnishes the true criterion of chemical equilibrium.

THERMODYNAMIC EQUATIONS

The four important thermodynamic properties, total internal energy E , enthalpy or heat content H , free energy F , and maximum total work A are termed the *thermodynamic potentials*.

The significance of the thermodynamic potentials can be visualized by referring to a particular chemical system. For example, the reaction of zinc metal in a solution of hydrochloric acid may be considered, assuming that the reaction takes place in a calorimeter at constant temperature involving the solution of 1 gram-atom of zinc in excess hydrochloric acid of a given initial concentration with no evaporation of solution. If the reaction proceeds at constant pressure, the heat given up to the calorimeter is equal to $-\Delta H$. At constant volume the heat to the calorimeter is $-\Delta E$. Both these reactions are extremely irreversible.

If it were possible to connect the zinc through an external electrical circuit with an insoluble cathode placed in the same solution and allow the reaction to proceed slowly and reversibly at constant pressure, the electrical energy developed would be $-\Delta F$. The change in heat content ΔH would still remain the same, but the heat given up to the calorimeter would be $T\Delta S$ and not $-\Delta H$. The electrical work plus the work of expansion done by the hydrogen evolved from the reaction would be the maximum total work and equal to $-\Delta A$.

In any reaction the values of ΔH , ΔE , ΔF , and ΔA depend only upon initial and final conditions and are independent of the path pursued, but the direct calorimetric or electrical measurements of these quantities must be made under conditions of change similar to those described above.

Differentiation of the Thermodynamic Potentials. From the definitions of the thermodynamic potentials and the first and second laws of thermodynamics it is possible to develop many relationships of great importance. These relationships are basically sound and rigorously applicable to all substances and systems under all conditions.

A few of the more important relationships are developed in the following sections, and by similar methods many others are possible. More extensive developments will be found in books devoted entirely to thermodynamics.

If consideration is limited to processes in which the only external force is pressure and the term w_f of Equation (1), Chapter V, is zero, the definitions of the thermodynamic potentials may be written in differential form as follows:

$$dE = dq - dw_e = T dS - p dV \quad (12)$$

$$dH = dE + d(pV) = dE + p dV + V dp \quad (13)$$

$$dF = dH - d(TS) = dH - T dS - S dT \quad (14)$$

$$dA = dE - d(TS) = dE - T dS - S dT \quad (15)$$

Substituting (12) in (13)

$$(16)$$

Substituting (16) in (14)

$$V dp \quad (17)$$

Substituting (12) in (15)

$$dA = -S dT - p dV \quad (18)$$

By restricting (16) to constant pressure an expression is obtained for the effect of temperature on enthalpy. Thus,

$$\left(\frac{\partial H}{\partial T} \right)_p \quad (19)$$

Also

$$\left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial S}{\partial p} \right)_T + V \quad (20)$$

Similarly, from (17), expressions are obtained for the effect of temperature and pressure on free energy.

$$\left(\frac{\partial F}{\partial T} \right)_p = -S = \frac{F - H}{T} \quad (21)$$

$$\left(\frac{\partial F}{\partial p} \right)_T = V \quad (22)$$

Equations (12) to (18) are exact differential equations representing continuous single-valued relationships between three variables of the form,

$$dz = M dx + N dy \quad (23)$$

It is necessary that

$$M = \left(\frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N =$$

if the differential is exact. Therefore, in any exact differential equation of the form of (23)

$$\left(\frac{\partial y}{\partial x} \right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial x}{\partial y} \right)_y = \frac{\partial^2 z}{\partial y \partial x}$$

or

$$\left(\frac{\partial M}{\partial y} \right)_x = \quad (24)$$

Applying the principle of Equations (23) and (24) to (17)

(25)

Combining (25) with (20) gives a more useful relationship between enthalpy and pressure which involves only specific volume and thermal expansion data. Thus,

Similarly, combining (23), (24), and (18)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial T}{\partial T}\right)_T$$

This is the thermodynamic form of the well-known Clapeyron equation. In applying (27) to the vaporization of a liquid the restriction of constant volume may be omitted because the vapor pressure is unaffected by volume. Since vaporization is a reversible process at constant pressure and temperature $\Delta S = \Delta H/T$ and

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = T(v_g - v_l)$$

where

ΔH = molal heat of vaporization = L_v

v_g = molal volume of vapor

v_l = molal volume of liquid

This is the usual form of the Clapeyron equation referred to on page 68.

By these same methods many other valuable relationships may be derived merely from application of mathematical principles to the basic equations of the thermodynamic potentials.

Change of Free Energy with Temperature. One of the most important relations desired in chemical thermodynamics is the variation in the change of free energy of a reaction with change in temperature at constant pressure. Such a relationship is expressed by Equation (21), but a more convenient form is derived as follows. This relationship is essential in establishing the effect of temperature on conditions of equilibrium in chemical processes.

From Equation (4)

$$\frac{\Delta F}{T} = \frac{\Delta H}{T} - \Delta S \quad (29)$$

$$\left(\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T}\right)_p = T\left(\frac{\partial T}{\partial T}\right)_p - \frac{\Delta H}{T^2} - \left(\frac{\partial T}{\partial T}\right)_p$$

By Equation (19)

$$\left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

or

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = T \left(\frac{\partial \Delta S}{\partial T}\right)_p \quad (31)$$

hence

$$\left(\frac{\partial \left(\frac{\Delta F}{T}\right)}{\partial T}\right)_p = -\frac{\Delta H}{T^2} \quad (32)$$

PROBLEMS

1. Calculate the increase in entropy when 1 lb of ice at 0° F and atmospheric pressure is converted to steam at 220° F and 1 atmosphere pressure.

2. The volume coefficient of expansion of water is 0.00465 cc per °C at 0° C. Calculate the increase in entropy when the pressure is reduced from 100 to 1 atmospheres, neglecting the effect of pressure on volume.

3. Derive differential equations for the following relationships:

- Variation of maximum total work A with temperature at constant volume.
- Change of enthalpy H with entropy S at constant pressure.
- Change of total energy E with volume at constant entropy S .
- Change of temperature with volume at constant entropy S .

CHAPTER XIII

FUGACITY AND THERMAL PROPERTIES AT HIGH PRESSURES

In dealing with reacting systems and with systems in equilibrium, both chemical and physical, it is of great value to define quantitatively what may be termed the *escaping tendency* of each component of the system. It is requisite for equilibrium in heterogeneous systems, such as a liquid and its vapors, that this escaping tendency of each component be equal in all phases. Where this equality does not exist the component will escape from the phase in which its escaping tendency is higher to the phase in which it is lower until equality and equilibrium are reached. This force or escaping tendency which reaches equality at equilibrium is a criterion of equilibrium and hence must be related to free energy change, which is also a universal criterion of equilibrium.

At conditions of low pressure, where the simple gas law is valid, the escaping tendency of each gaseous component is satisfactorily represented by its partial pressure as defined in Chapter III. Thus, in equilibrium at low pressure between liquids and their vapors the partial pressures exerted by each component will be equal in all phases. For example, if a system of benzene, water, and air is in equilibrium, the partial vapor pressure of the water in the benzene phase will be equal to the partial pressure of water vapor in the gas phase which in turn will be equal to the vapor pressure of the water in the water phase. The same situation prevails with respect to the benzene and air.

When conditions of temperature and pressure are such that behavior of gases is not ideal, the escaping tendency is no longer quantitatively represented by the partial pressure. For a universally applicable treatment of such cases an important property termed the *fugacity* has been mathematically defined¹ by the following equation to represent correctly the escaping tendency

$$dF = RT d \ln f \quad (1)$$

or

$$F = RT \ln f + B$$

where

F = molal free energy

f = fugacity

B = an integration constant

¹ G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill (1923).

When the fugacity changes isothermally from state 1 to state 2

$$\Delta F = F_1 - F_2 = \frac{f_1}{f_2} \quad (2)$$

At equilibrium $f_1 = f_2$; hence this equation for fugacity satisfies the universal condition of equilibrium that $\Delta F = 0$.

Fugacities of Gases and Vapors. From Equation (22), page 421

$$\frac{\partial \ln f}{\partial p} = v$$

Combining this with Equation (1)

$$\left(\frac{\partial \ln f}{\partial p} \right)_T = \frac{v}{RT} \quad (3)$$

From Equation (17) page 392,

$$pv = CRT$$

where C is the compressibility factor. Hence

$$d \ln f = C d \ln p \quad (4)$$

From Equation (4) for ideal gases where $C = 1.0$, $d \ln f = d \ln p$, and it is evident that fugacity has the same units as pressure. Thus fugacity may be looked upon as a corrected pressure or vapor pressure so defined as to represent accurately the escaping tendency and to be directly related to free energy. In order to assign it a definite numerical scale the fugacity is arbitrarily made equal to pressure at zero pressure where gaseous behavior is ideal or $f/p = 1.0$ where $p = 0$. Thus,

$$\begin{aligned} d \ln \frac{f}{p} &= C d \ln p - d \ln p = (C - 1) d \ln p \\ \ln \frac{f}{p} &= \int_0^p (C - 1) d \ln p = \int_0^p \frac{(C - 1)}{p} dp \end{aligned} \quad (5)$$

A graphical integration of Equation (5) may be made by combining it with Fig. 83, which expresses the compressibility factor as a function of reduced pressure and reduced temperature. Various workers¹ have carried out this integration which results in a generalized relationship between fugacity, reduced temperature, reduced pressure, and pressure. This relationship is conveniently presented by plotting the ratio of fugacity to pressure (f/p) against reduced temperature and pressure

¹ Selheimer, Souders, Smith, and Brown, *Ind. Eng. Chem.* **26**, 514 (1932); Lewis and Luke, *Trans. Am. Soc. Mech. Engr.* **54**, 55 (1932), *Ind. and Eng. Chem.* **25**, 725 (1933); R. H. Newton, *Ind. and Eng. Chem.* **27**, 302 (1935).

The ratio f/p is termed the *activity coefficient* and is equal to unity where the simple gas law is valid.

Average values of the activity coefficients of gases are plotted in Fig. 87 developed by Watson and Smith. This chart was derived from the same data on which Fig. 83 was based. For many purposes these charts may be taken as applicable to all gases. The errors involved will generally be less than 10 per cent. Where more precise data are required the integration of Equation (5) may be carried out for a specific substance if the necessary compressibility data are available.

As pointed out on page 399, when applying reduced relationships to hydrogen and helium, the reduced temperature should be calculated by adding 8 to the critical temperature in degrees K and the reduced pressure by adding 8 to the critical pressure in atmospheres.

The fugacity of any gas or vapor at specified conditions is readily obtained when its critical temperature and pressure are known.

Illustration 1. Calculate the fugacity of methane at 40° F and 1000 lb per sq in. gauge.

From Table XIX, $T_c = -116.5^\circ \text{ F}$ and $p_c = 673 \text{ lb per sq in.}$

$$\text{Reduced temperature} = \frac{40 + 460}{-116.5 + 460} = 1.40$$

$$\text{Reduced pressure} = \frac{1014.7}{673} = 1.51$$

Activity coefficient (Fig. 87) = 0.86

$$\text{Fugacity} = +1014.7 \times 0.86 = 872 \text{ lb per sq in.}$$

Fugacities of Liquids. From the basic concept of fugacity as a measure of escaping tendency it follows that the fugacity of a liquid must be equal to that of its vapor in equilibrium with it. Thus when a liquid is in equilibrium with its pure vapor the fugacity of a liquid is determined by calculating the fugacity of the vapor at the equilibrium temperature and pressure by the above method.

Illustration 2. Calculate the fugacity of liquid benzol in equilibrium with its pure vapor at a temperature of 500° F. The critical temperature of benzene is 550° F and the critical pressure is 700 lb per sq in. The vapor pressure at 500° F is 490 lb per sq in.

$$\text{Reduced temperature} = \frac{500 + 460}{550 + 460} = 0.95$$

$$\text{Reduced pressure} = 490/700 = 0.70$$

Activity coefficient (Fig. 87) = 0.69

$$\text{Fugacity of vapor} = \text{fugacity of liquid} = 490 \times 0.69 = 338 \text{ lb per sq in.}$$

It was pointed out in Chapter IV, page 79, that the vapor pressure of a liquid is affected by the total pressure on its surface when this total pressure is not equal to the vapor pressure. Similarly, the fugacity of

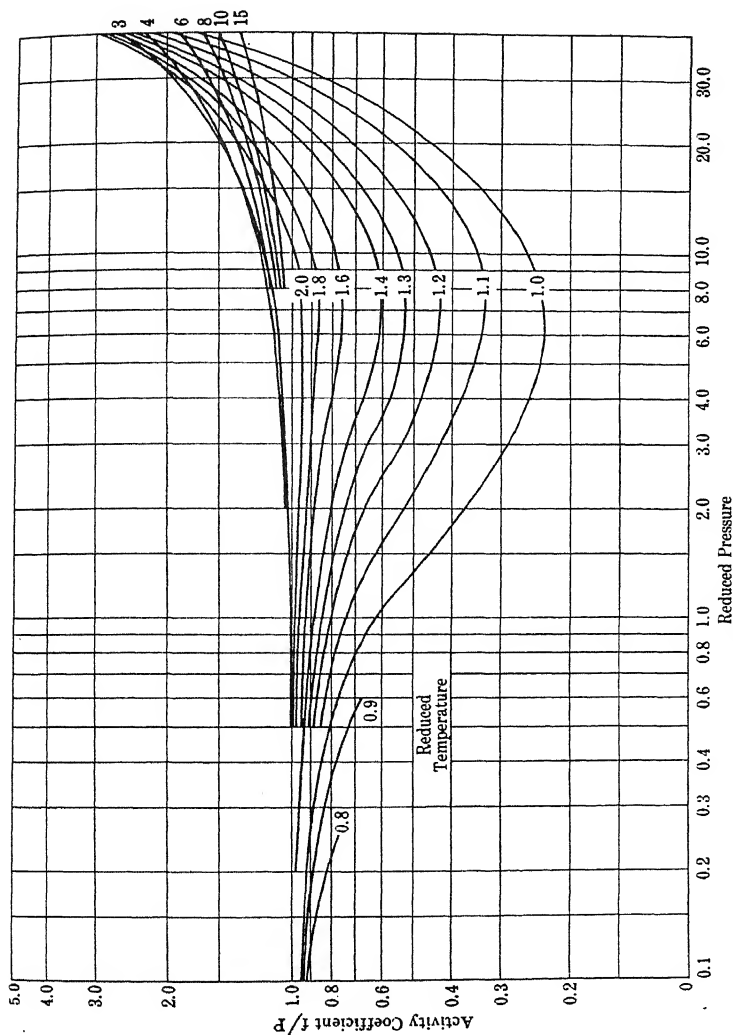


Fig. 87. Activity Coefficients of Gases and Vapors.

the liquid state is a function of total pressure and is correctly expressed by Equation (3). Since the molal volume of the liquid v is little affected by pressure except in the critical region this equation may be integrated to give

$$\ln \frac{f_p}{f_n} = \frac{v(p - p_n)}{RT} \quad (6)$$

where f_p = fugacity at total pressure p
 f_n = fugacity at normal vapor pressure p_n

Equation (6) permits ready calculation of the fugacities of liquids at any total pressure.

Illustration 3. Calculate the fugacity of liquid benzol under the conditions of Illustration 2 if the liquid is in an atmosphere of hydrogen such that the total gauge pressure is 2000 lb per sq in. The density of liquid benzol at these conditions is 0.57 gram per cubic centimeter.

$$\text{Molal volume } v = \frac{78}{0.57 \times 62.4} = 2.2 \text{ cu ft per lb-mol}$$

Substituting in Equation (6)

$$\ln \frac{f_p}{338} = \frac{2.2(2015 - 490)}{10.71 \times (500 + 460)} = 0.326$$

$$\log f_p/338 = 0.326 \times 0.434 = 0.141 \text{ or } f_p/338 = 1.38$$

$$f_p, \text{ the fugacity at 2000 lb per sq in.} = 1.38 \times 338 = 467 \text{ lb per sq in.}$$

Effect of Temperature on Fugacity. The following equation is derived by the method of Lewis and Randall¹ to relate fugacity to temperature.

A substance in a given state at temperature T , pressure p , molal free energy F , fugacity f , and molal enthalpy H , is compared to the same substance at the same temperature but at a low pressure where the free energy is F^* and the fugacity f^* is equal to the pressure. Under these conditions the enthalpy H^* is independent of pressure. From Equation (3)

$$F^* - F = RT \ln \frac{f^*}{f} = RT (\ln f^* - \ln f) \quad (7)$$

Differentiating with respect to temperature at constant pressure

$$\left(\frac{\partial F^*}{\partial T}\right)_p - \left(\frac{\partial F}{\partial T}\right)_p = R \ln \frac{f^*}{f} + RT \left(\frac{\partial \ln f^*}{\partial T}\right)_p - RT \left(\frac{\partial \ln f}{\partial T}\right)_p \quad (8)$$

Since f^* is equal to pressure,

$$\left(\frac{\partial F^*}{\partial T}\right)_p = R \ln \frac{p}{f} + RT \left(\frac{\partial \ln p}{\partial T}\right)_p$$

¹ Lewis and Randall "Thermodynamics," p. 200, McGraw-Hill (1923).

Combining (7) and (8)

$$\left(\frac{\partial F}{\partial T}\right)_p = \frac{F^*}{T} - \frac{F}{T} \quad (9)$$

Combining (9) with Equations (3) and (21), Chapter XII,

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = \frac{H^* - H}{RT^2} \quad (10)$$

where

H = molal enthalpy at an elevated pressure p , and temperature T

H^* = molal enthalpy at the same temperature T but at a pressure sufficiently low that the gas behaves ideally.

Effect of Pressure on Enthalpy of Gases and Vapors. Since at constant pressure the fugacity is proportional to the activity coefficient the above Equation (10) may be written

$$\left(\frac{\partial T}{\partial T}\right)_p = \frac{H^* - H}{RT^2} = \frac{\Delta H^*}{RT^2} \quad (11)$$

where

γ = the activity coefficient p

Since $T_r = T/T_c$

$$\left(\frac{\partial \ln \gamma}{\partial T}\right)_p = \frac{1}{T_c} \left(\frac{\partial \ln \gamma}{\partial T_r}\right)_p = \frac{\Delta H^*}{RT^2} \quad (12)$$

where T_r is the reduced temperature and T_c the critical temperature. Rearranging (12)

$$\frac{1}{T_c} \left(\frac{\partial \ln \gamma}{\partial T_r}\right)_p = \frac{\Delta H^*}{T^2} \quad \text{or} \quad R \left(\frac{\partial \ln \gamma}{\partial \ln T_r}\right)_p = \frac{\Delta H^*}{T}$$

Values of $\left(\frac{\partial \ln \gamma}{\partial \ln T_r}\right)_p$ were determined by Watson and Smith¹ replotting the data of Fig. 87 and graphically differentiating the logarithm of the activity coefficient with respect to the logarithm of reduced temperature.

The results are expressed in Fig. 88 plotting the term $\frac{\Delta H^*}{T}$ as a function of reduced temperature and reduced pressure.

The enthalpy of any substance at elevated pressure is readily estimated from Fig. 88 and its enthalpy at atmospheric pressure. The correction ΔH^* read from the chart is merely subtracted from the value of enthalpy at low pressure.

Illustration 4. Calculate the enthalpy in Btu per pound of carbon dioxide at 200° F and a gauge pressure of 300 lb, referred to 60° F and atmospheric pressure.

¹ K. M. Watson and R. L. Smith, National Petroleum News, July, 1936.

Mean molal heat capacity at atmospheric pressure, between 60° and 200° F (Fig. 14) = 9.3.

Enthalpy at 200° F, 1.0 atm = $9.3 \times 140/44 = 29.6$ Btu per lb

Reduced temperature at 200° F = $660/548 = 1.185$

Reduced pressure at 300 lb = $315/73 \times 14.7 = 0.294$

$$\frac{\Delta H^*}{T} \text{ (Fig. 88) } = 0.45$$

$$\frac{\Delta H^*}{M} = \frac{0.45 \times 660}{44} = 6.8 \text{ Btu per lb}$$

$$\text{Enthalpy at 200° F, 300 lb per sq in.} = 29.6 - 6.8 = 22.8$$

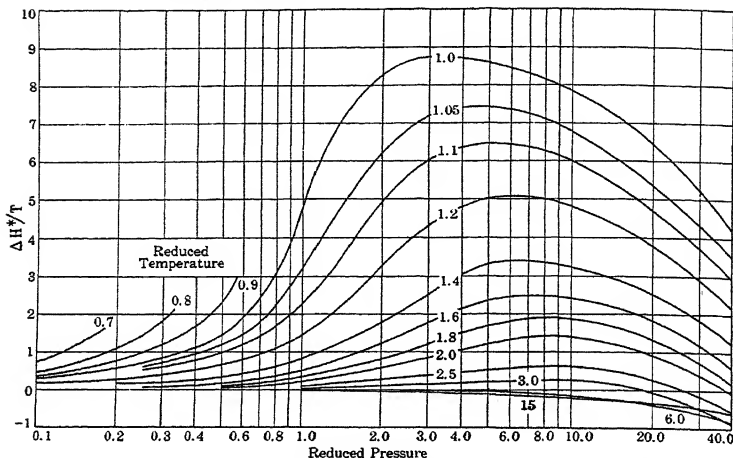


Fig. 88. Enthalpy-Pressure Relationship for Gases and Vapors.

Joule-Thomson Effect. Equation (11) is also adapted to calculating the change in temperature occurring when a gas is freely expanded from an elevated to atmospheric pressure. This temperature change in isoenthalpic expansion is termed the Joule-Thomson effect. The temperature difference, ΔT^* , is given by the following equation derived from Equation (13).

$$\frac{\Delta H^*}{c_p} = \left(\frac{\delta \ln \gamma}{\delta \ln T_R} \right)_p \frac{RT}{\alpha} \quad (14)$$

where

c_p = mean molal heat capacity at atmospheric pressure between the initial and final temperatures

ΔT^* = change in temperature accompanying free expansion from an elevated pressure to a low pressure at which enthalpy is independent of pressure

Ordinarily, where the Joule-Thomson effect is not large, the heat capacity may be taken at the initial temperature without serious error. If further accuracy is required successive approximations may be made assuming the final temperature as a first approximation and correcting it by calculation.

Illustration 5. Calculate the temperature change if the carbon dioxide of Illustration 4 is expanded to atmospheric pressure.

As a first approximation assume the average temperature to be 190° F with a corresponding heat capacity of 9.45 Btu per lb-mol °F, from Fig. 13.

$$-\Delta T^* = 6.8 \times 44/9.45 = 31.7^\circ \text{ F}$$

A negligible error results from taking the average heat capacity at 190° F instead of the correct average temperature of 184° F.

Effect of Pressure on Enthalpy of Liquids. The effect of change of pressure at constant temperature on the enthalpy of any substance is given by Equation (26), Chapter XII

$$= V - T \left(\frac{\delta V}{\delta T} \right)_p \quad (15)$$

where H is the enthalpy of the quantity of substance occupying volume V . From this equation the change of enthalpy of a liquid with pressure may be calculated if data on thermal expansion and compressibility are available. This correction is negligible in the case of liquids at the pressures encountered in common industrial practice, except in the critical region.

In dealing with liquids near the critical temperature calculation of enthalpy at any pressure becomes difficult because of the uncertain variation of heat capacity with pressure. Few data are available at these conditions on either heat capacities of liquids or the expansion and compressibility relationships necessary for their extension to various pressures. For this reason the problem of estimating enthalpies of liquids near the critical point is best handled by the indirect method described in the next section.

Enthalpy Charts. Where the enthalpy of a particular substance is frequently required, considerable saving in time will result from the construction of an enthalpy chart relating enthalpy to temperature and pressure as in Fig. 89 for benzol. Such a chart is readily constructed for gases and vapors by the methods illustrated previously. By use of this chart the tedious calculations of variation of heat capacity with pressure and temperature are eliminated and all high-temperature and high-pressure thermal calculations are handled by direct readings on the chart. Joule-Thomson effects may be read directly from the chart

for changes in pressures in any range. The enthalpy chart is particularly valuable for calculations involving vaporization accompanied by pressure and temperature changes.

In the construction of the chart the enthalpy curve for atmospheric pressure is first derived from specific heats and heats of vaporization as described in Chapter V. The curves for higher pressures in the 100 per cent vapor region are then derived from this by means of Fig. 88. These curves each extend downward to the saturation temperature at the corresponding pressure where they drop vertically to the enthalpy of the liquid. The difference between the enthalpy of the saturated

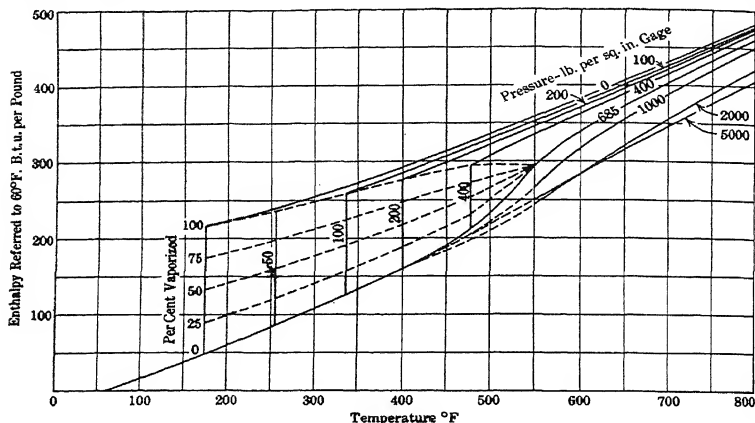


FIG. 89. Temperature-Enthalpy Diagram for Benzol (C_6H_6).

vapor and the enthalpy of liquid at the same temperature and pressure is by definition the heat of vaporization at that particular temperature and pressure. This may be estimated from the heat of vaporization at the normal boiling-point and Fig. 25, page 140. The enthalpy of the liquid is then obtained by subtracting the heat of vaporization from the enthalpy of the saturated vapor. Pressure has only a slight effect on the enthalpy of the liquid except in the critical region, and it will be found that points for the enthalpy of the liquid at its boiling-point under different pressures lie practically on a single smooth curve until the critical temperature is approached. In this region enthalpies of the liquid at pressures higher than the critical may be estimated by joining the enthalpy of the vapor curves smoothly to the curve representing the enthalpy of the boiling liquid as shown by the broken line curves of

Fig. 89. This method has the advantage of giving a good approximation to the correct enthalpy without consideration of the effect of pressure on the enthalpy of the liquid, which is a tedious and uncertain calculation as indicated on page 431.

Illustration 6. Calculate the enthalpy of saturated benzol vapor under an absolute pressure of 400 lb per sq in. referred to the liquid at 60° F and 1.0 atmosphere. Also calculate the enthalpy of the liquid at the same conditions.

From Fig. 3 the boiling-point of benzol at 400 lb per sq in. (20,600 mm) is 245° C or 472° F.

Normal boiling-point =	175° F
Critical pressure =	701 lb per sq in.
Critical temperature =	551° F

The first step is to calculate the enthalpy of the vapor at atmospheric pressure and 472° F.

Mean specific heat of liquid from 60° to 175° F (Fig. 39, page 219, using $K = 9.8$) =	0.42
Heat content of liquid =	48.8 Btu per lb
Mean specific heat of vapor from 175° to 472° F (Fig. 40, page 220) =	0.367
Heat content of vapor =	111 Btu per lb
Heat of vaporization at 175° F (Equation 46, page 139) =	167
Enthalpy of vapor at 472° F, 1.0 atm =	327 Btu per lb

The enthalpy of the vapor is then corrected to the higher pressure by means of Fig. 88.

Reduced temperature =	0.92
Reduced pressure =	0.57
$\Delta H^*/T$ =	2.7
$\Delta H^*/M$ =	32 Btu per lb
Enthalpy of vapor at 472° F, 400 lb per sq in. =	295 Btu per lb

To obtain the enthalpy of the liquid the heat of vaporization at 472° F is subtracted from the enthalpy of the vapor. Referring to Fig. 25, page 140.

$$\begin{array}{ll} T_B/T_C = 0.630 & T/T_B = 1.475 \\ \gamma = 0.335 & L_B = 167.5 \end{array}$$

Latent heat at 472° F =	82.8 Btu per lb
Enthalpy of liquid at 472° F = 295 - 82.8 =	212 Btu per lb

Additional calculations for the derivation of an entire diagram such as Fig. 89 are made in exactly the same manner as the above illustration.

It must be emphasized that the generalized method presented above is not rigorously correct for any substance, but is an approximation satisfactory for use in many cases where specific data are not available. For many substances such as steam, ammonia, carbon dioxide, and other refrigerants enthalpy data are available which have been derived from

specific data by more exact methods. Use of such data when available is preferable.

Heat Capacities of Gases at High Pressures. As pointed out in Chapter V, page 113, pressure has a large effect on the heat capacity of a gas or vapor at high pressures.

By rearranging Equation (12) Watson and Smith developed a generalized expression for the difference between heat capacity at an elevated pressure and heat capacity at a low pressure and the same temperature. Thus, using the symbols of Equation (12), since

$$c_p = \left(\frac{\partial H}{\partial T} \right)_p \quad \text{and} \quad H^* - H = T \left(\frac{H^* - H}{T} \right) = T \left(\frac{\Delta H^*}{T} \right)$$

$$c_p^* - c_p = \frac{\Delta H^*}{T} + T \frac{\delta \left(\frac{\Delta H^*}{T} \right)}{\delta T} = \frac{\Delta H^*}{T} + \frac{\delta \left(\frac{\Delta H^*}{T} \right)}{\delta \ln T}$$

or, since

$$T = T_r T_c$$

$$c_p^* - c_p = \frac{\Delta H^*}{T} + \frac{\delta \left(\frac{\Delta H^*}{T} \right)}{\delta \ln T_r}$$

where

c_p^* = molal heat capacity at a low pressure below which heat capacity is unaffected by change in pressure

c_p = molal heat capacity at elevated pressure and same temperature

Equation (17) expresses the difference between heat capacities at low and high pressures as a function of reduced temperature and reduced pressure obtained by differentiating the relationship expressed by Fig. 88. If the theorem of corresponding states were entirely rigorous the resulting relationship would be exact for all materials. However, as was previously pointed out, this principle is but an approximation. In the successive differentiations required in arriving at Equation (17) these inaccuracies are apparently magnified and actual experimental data on various substances show considerable deviation from Equation (17).

In Fig. 90 is plotted a chart based on Equation (17) and subject to its limitations. This chart was derived by a graphical differentiation of Fig. 88 together with experimental data on the effect of pressure on the heat capacities of air, nitrogen, carbon dioxide, and water vapor. It will be noted that the effect of pressure is very large, especially in the critical region. The corrections obtained from this chart may be as much as 50 per cent in error for some materials in certain regions.

However, at present it is believed to be the best general method available for approximating this correction where specific data are not available.

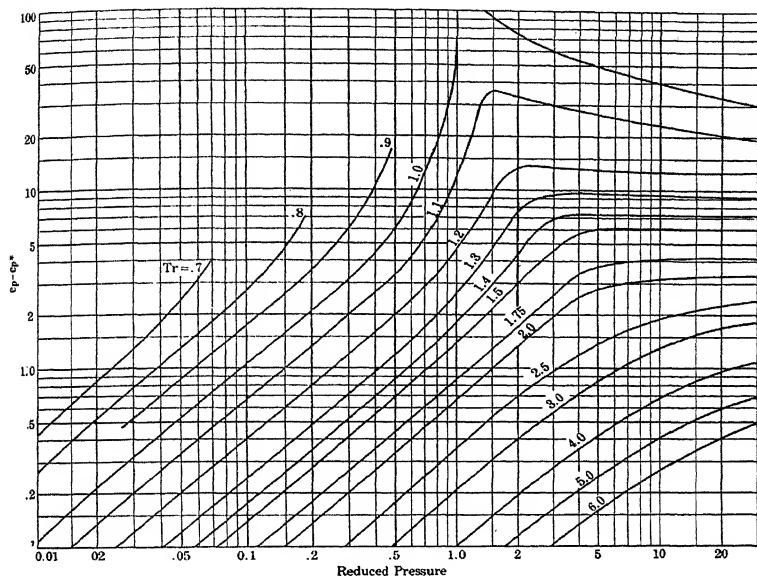


FIG. 90. Effect of Pressure on Molal-Heat Capacity of Gases.

Illustration 7. Estimate the heat capacity of carbon dioxide at a temperature of 100°C and a gauge pressure of 1000 lb per sq in.

$$\begin{aligned}
 \text{Reduced pressure} &= \dots\dots\dots 1015/14.7 \times 73 = 0.945 \\
 \text{Reduced temperature} &= \dots\dots\dots 373/273 + 31 = 1.23 \\
 c_p - c_p^* \text{ (Fig. 90)} &= \dots\dots\dots 3.5 \\
 c_p^* \text{ (Fig. 11)} &= \dots\dots\dots 9.55 \\
 c_p &= 9.55 + 3.5 = \dots\dots\dots 13.05
 \end{aligned}$$

Effect of Pressure upon the Heat of Reaction at Constant Pressure. As explained in Chapter VI, the heat of reaction at 18°C and atmospheric pressure is obtained directly from heats of formation. For any other temperature conditions it is necessary to add the heat content of reactants and subtract the heat content of products. At high pressures it is necessary to consider the change in heat content of reactants and products with increase in pressure as well as temperature. The de-

creased heat content of gases with increase in pressure is related in Fig. 88 to reduced temperatures and reduced pressures. For condensed systems, solids, liquids, and solutions, this correction is usually negligible since the effect of pressure upon heat content is very small as pointed out on page 431.

Where a reaction proceeds with change in pressure it is not possible to calculate accurately the heat evolved from changes in heat content unless the path of pressure change is known, that is, unless the amount of external work performed by or upon the gas during the pressure change is known. Only when reactions proceed at constant pressure is the heat evolved equal to the loss in heat content or enthalpy.

Illustration 8. Calculate the heat of combustion of carbon to carbon dioxide at a pressure of 100 atmospheres where the reactants enter at 18° C and the products leave at 100° C. The standard heat of combustion is 94,400 calories per gram-mol.

Heat Content of Reactants (referred to 18° C and 1 atm): The heat content of solid carbon at 18° C and 100 atmospheres is negligible.

For oxygen:

Reduced temperature = $(18 + 273)/154 =$	1.89
Reduced pressure = $100/49.7 =$	2.01
$\Delta H^*/T$ (Fig. 88) =	0.70
$\Delta H^* = 0.70 \times 291 =$	204 cal per gram-mol

Therefore the heat content of the oxygen is -204 cal per gram-mol.

Heat content of CO₂ (referred to 18° C and 1 atm)

Reduced temperature = $373/304 =$	1.23
Reduced pressure = $100/73 =$	1.37
$\Delta H^*/T$ (Fig. 88) =	2.0
$\Delta H^* = 2.0 \times 373 =$	746 cal per gram-mol
Heat content at 100° C and 1.0 atm	
= $(100 - 18)(9.36) =$	767 cal per gram-mol
Heat content at 100° and 100 atm	
= $767 - 746 =$	21 cal per gram-mol

Substituting in Equation (10), page 204

$Q = 94,400 + (-204) - 21 = 94,175$ cal per gram-mol, the heat evolved in the above reaction.

Where the standard heat of reaction is small the relative importance of the pressure correction to the heat of reaction is much greater.

PROBLEMS

- Calculate the fugacities of the following gases:
Air at 60° F and 100 atmospheres.
Ammonia at 80° C and 40 atmospheres.
Carbon dioxide at 150° F and a gauge pressure of 2000 lb per sq in.
- Calculate the fugacity of liquid ethylene in contact with its saturated vapor at 0° C and 40.6 atmospheres.

3. Calculate the fugacity of liquid chlorine in contact with a mixture of hydrogen and its own vapors at a temperature of 122° F and a pressure of 1000 lb per sq in. absolute. The vapor pressure of chlorine at this temperature is 14.1 atmospheres.
4. Calculate the enthalpy of steam at 500° F and a gauge pressure of 400 lb per sq in. referred to liquid water at 32° F under its own vapor pressure.
5. Calculate the temperature change in free expansion of butane from 212° F and 200 lb per sq in. gauge to atmospheric pressure. The critical temperature is 151° C, and the critical pressure 28,500 mm of Hg.
6. Develop an enthalpy chart for heptane liquid and vapor in the range from 60° F to 700° F and from atmospheric pressure to 1000 lb per sq in. Plot enthalpy in Btu per pound referred to 60° F as ordinates and temperature as abscissas with lines of constant pressure at atmospheric, 100, 200, 400, 700, and 1000 lb per sq in. gauge. The properties of heptane (C_7H_{16}) are as follows:

Boiling-point.....	98.4° C
Specific gravity at 15° C.....	0.684
Critical temperature.....	266.8° C
Critical pressure.....	26.8 atm

7. Calculate the heat of reaction in the synthesis of ammonia at a pressure of 300 atmospheres and a temperature of 700° K. (For calculating the reduced conditions of hydrogen see page 399.)

CHAPTER XIV

CHEMICAL EQUILIBRIA

As explained in Chapter XII the criterion of equilibrium in a chemically reacting system is that the change in free energy of any possible process shall equal zero. A negative free energy change may be looked upon as the driving potential which is directing the reaction towards a state of rest and as a direct measure of the departure of the reacting system from its equilibrium state. From a kinetic viewpoint the reaction at equilibrium may still be considered as proceeding reversibly back and forth but with equal rates in opposite directions and with no net change in composition.

From an industrial viewpoint it is of importance to relate the change in free energy of a reacting system to the composition of the equilibrium mixture in order to determine the extent of conversion of the initial reactants. Such considerations are essential in determining the most favorable conditions of temperature, pressure, and composition in order to obtain the greatest conversion of reactants and the highest yield of products.

It is the objective of this chapter to develop applications of free energy data to chemical reactions. The complex treatment of reactions involving solutions of electrolytes is beyond the scope of this book and will be found in the more extensive textbooks on chemical thermodynamics.

ACTIVITY

In Chapter XIII the fugacity was defined as a quantitative measure of the escaping tendency equivalent to a corrected pressure directly related to free energy by the relation, $F = RT \ln f + \text{constant}$. For treatment of problems in chemical equilibrium it is convenient to define another new property directly related to fugacity and hence also to free energy. This property, called activity, a , is defined as the ratio of the fugacity of a material in a given state to its fugacity in an arbitrarily defined *standard state* at the same temperature. Thus,

$$a = \frac{f}{f^\circ} \quad (1)$$

where

a = activity

f = fugacity in the given state

f° = fugacity in the standard state at the same temperature.

Combining (1) with Equation (1), Chapter XIII

$$RT \ln a = F - F^\circ \quad (2)$$

where

F = molal free energy in given state at temperature T

F° = molal free energy in the standard state at the same temperature T

Just as fugacity is a corrected unit for pressure so *activity is a corrected unit for expressing concentration* by the simple thermodynamic relation of Equation (2).

Standard States for Activities. The choice of the standard states necessary to complete the definition of activity is arbitrary since it affects only the numerical magnitude of the function and not its relationship to other properties. It is, however, desirable to select standard states such that the resulting numerical scales will be convenient and equal to common expressions of concentration in ideal systems. The following standard states are those adopted by Lewis and Randall¹ and are in general use.

In the case of a *gas or vapor* it is most convenient to define the *standard state as that of unit fugacity, $f^\circ = 1$* . With this selection of the standard state the *activity of a gas is equal to its fugacity*. If a *liquid or solid* is involved in a process as a pure substance or in the rôle of a solvent it is convenient to select the *pure substance at one atmosphere pressure* as the standard state. With this reference the activity of a pure liquid or pure solid at one atmosphere pressure is unity. Where a liquid or solid is considered as the solute as in dilute solutions it is convenient to define the standard state such that as the solution approaches an infinite dilution the ratio of activity to mol fraction of solute is equal to unity, $a/N = 1$.

Activity of Gases in Mixtures. For a pure gas, the activity is numerically equal to its fugacity, or $a = f$. At low pressures where the simple gas law applies the fugacity is equal to pressure, and activity is also equal to pressure, or $a = f = p$. Similarly, in gaseous mixtures the activity of any component gas is equal to the fugacity of that component gas, or $a_B = f_B$. At conditions such that the simple gas law is applicable, the fugacity of a component gas is equal to its partial pres-

¹ "Thermodynamics," McGraw-Hill (1923).

sure, or $f_B = p_B$, and the activity of a component gas is equal to its partial pressure, or $a_B = f_B = p_B$. The subscripts in each case refer to component B .

Lewis and Randall have defined a *perfect solution* as one in which the fugacity of any component is equal to its mol fraction times its fugacity in the pure state at the same temperature and pressure. Thus,

$$f_B = f'_B N_B \quad (3)$$

where

f_B = fugacity of component B in the solution

f'_B = fugacity of pure component B at the temperature and pressure of the solution.

N_B = mol fraction of B .

Equation (3) is sometimes termed the Lewis and Randall *fugacity rule*.

When applied to a mixture of gases Equation (3) has been shown¹ to be equivalent to assuming the additive volume law of Amagat. As previously pointed out, this law is only an approximation and Equation (3) is hence not exact. However, it is a satisfactory approximation for many systems even at high pressures and is of a higher order of accuracy for gaseous mixtures than the ideal gas law. By definition, from Chapter XIII,

$$f'_B = p \gamma_B \quad (4)$$

where

p = total pressure

γ_B = activity coefficient of component B at the temperature and total pressure of the system

Since for gases activity is equal to fugacity, combining Equations (3) and (4),

$$a_B = \gamma_B N_B p \quad (5)$$

Where the fugacity rule applies the activity of component gas B is given by Equation (5). At low pressures, where the ideal gas law applies, γ_B is equal to unity and the activity becomes equal to the partial pressure or $a_B = N_B p = p_B$.

Activity of Liquids and Solids in Solution. The activity of a pure liquid or solid at one atmosphere pressure is taken as unity. For perfect solutions where the fugacity rule applies the activity of the solvent is equal to its mol fraction, or $a_1 = N_1$, where N_1 is the mol fraction of the solvent.

When a liquid or solid is considered as a solute in a dilute solution, the standard state is so defined that the activity equals the mol fraction

¹ Newton and Dodge, Ind. & Eng. Chem. 27, 577 (1935).

in dilution. Thus, where the fugacity rule applies the activity is equal to the mol fraction of solute, $a_2 = N_2$.

For solutions of strong electrolytes and all other liquid solutions where the fugacity rule is not applicable, activities may be calculated from experimental data by methods described by Lewis and Randall. Methods are described for measuring activities from vapor pressures, from the distribution of a solute between two solvents, from measurements of electromotive force, and from freezing-point determinations.

It must be remembered that the activity is a thermodynamic expression of concentration and is equal to the mol fraction only in case of ideal solutions or to partial pressures only in the case of ideal gases. Under actual conditions large deviations from the ideal may occur which for solutions are measured by the deviation of a/N from 1.0 and for gases by the deviations of a/p from 1.

Effect of Pressure upon Activity. The activity of a substance is primarily determined by its concentration and pressure. When the concentration of a component in a solution is increased its fugacity increases, as does its activity referred to a fixed standard state at the same temperature. Similarly the fugacity and also the activity are increased by an increase in pressure. From Equation (1), $\ln a = \ln f - \ln f^\circ$, and since f° is constant at a given temperature, $d \ln a = d \ln f$. Substituting in Equation (3) of Chapter XIII,

$$\bar{v} \ln a = \frac{v}{RT} \quad (6)$$

This equation expresses the variation of the activity with pressure. For liquids and solids the change in activity with pressure usually can be neglected except at high pressures.

FREE ENERGY CHANGES IN CHEMICAL REACTIONS

In Chapter XII it was pointed out that free energy is an extensive property and that the free energy change in any process is determined by final and initial conditions and not by the intermediate course of the process. Thus changes of free energy in chemical reactions may be handled by methods parallel to those demonstrated for calculating heats of reaction in Chapter VI. Tables of standard free energies of formation have been prepared giving the free energy change taking place in the formation of many compounds from the elements. From these data the free energy changes in reactions may be calculated from balances of the free energies of formation of the products and reactants, just as the heat of reaction was calculated from balances of the heats of formation.

Effect of Temperature on Free Energy Change. From Equation (32), Chapter XII,

$$\left(\frac{\partial \Delta F}{\partial T}\right)_p = -\frac{\Delta H}{T^2} \quad (7)$$

In applying this equation to the free energy change of a chemical reaction the variation of $-\Delta H$, the heat of reaction, with temperature is expressed by Kirchhoff's Equation (11), Chapter VII, where the heat capacity of each reactant and product may be expressed by the parabolic equation $C_p = a + bT + cT^2$. Thus, from Equation (14), Chapter VII,

$$\Delta H = \Delta H_0 - \frac{1}{2} \Delta b T^2 + \frac{1}{3} \Delta c T^3 \quad (8)$$

where ΔH_0 is an integration constant.

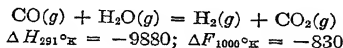
Combining (7) and (8) and integrating,

$$\frac{\Delta F}{T} = \frac{\Delta H_0}{T} - \Delta a \ln T - \frac{1}{2} \Delta b T - \frac{1}{6} \Delta c T^2 + I$$

$$\text{or} \quad \Delta F = \Delta H_0 - \Delta a T \ln T - \frac{1}{2} \Delta b T^2 - \frac{1}{6} \Delta c T^3 + I T \quad (9)$$

Equation (9) expresses the free energy change of a reaction at constant temperature and pressure as a function of temperature. For complete evaluation, heat-capacity data as a function of temperature must be available for each reactant and product. One value of ΔH at a given temperature must be known to establish ΔH_0 , and one value of ΔF at a given temperature to evaluate the integration constant I .

Illustration 1. Calculate the change in free energy of the water gas reaction proceeding at 25° C and at atmospheric pressure, using the heat-capacity data of the text.



The heat-capacity data for the gases involved expressed as a function of degree absolute are obtained from Table I, page 113.

$$\begin{aligned} \text{For } \text{CO}(g), c_p &= 6.761 + 0.000606T + 0.13 \times 10^{-6}T^2 \\ \text{H}_2\text{O}(g), c_p &= 8.217 + 0.000173T + 1.30 \times 10^{-6}T^2 \\ \text{H}_2(g), c_p &= 6.850 + 0.00028T + 0.22 \times 10^{-6}T^2 \\ \text{CO}_2(g), c_p &= 7.713 + 0.00526T - 0.83 \times 10^{-6}T^2 \end{aligned}$$

Combining the coefficients as required by Equation (13), Chapter VII

$$\begin{aligned} \Delta a &= -6.761 - 8.217 + 6.850 + 7.713 = -0.415 \\ \Delta b &= -0.000606 - 0.000173 + 0.00028 + 0.00526 = 0.00476 \\ \Delta c &= [-0.13 - 1.30 + 0.22 - 0.83] 10^{-6} = -2.04 \times 10^{-6} \end{aligned}$$

From Equation (14), Chapter VII,

$$+\Delta H T = \Delta a T + \frac{1}{2} \Delta b T^2 + \frac{1}{3} \Delta c T^3 + \Delta H_0$$

The integration constant ΔH_0 may be obtained by substituting the value of $-\Delta H_T$ at 291° K in this equation, where $-\Delta H_{291} = 9880$.

$$-9880 = -0.415(291) + 0.00238(291)^2 - 0.68 \times 10^{-6} (291)^3 + \Delta H_0$$

or
$$\Delta H_0 = -9944$$

At $T = 1273^\circ \text{K}$

$$\Delta H = -0.415(1273) + 0.00238(1273)^2 - 0.68(1273)^3 \cdot 10^{-6} - 9944$$

or
$$\Delta H = -8012$$

From Equation (8)

$$\Delta F = \Delta H_0 - \Delta aT \ln T - \frac{1}{2}\Delta bT^2 - \frac{1}{6}\Delta cT^3 + IT$$

The integration constant I may be obtained by substituting the known value of ΔF at 1000° K,

$$-830 = -9944 + 0.415(1000) \ln (1000) - 0.00238(1000)^2 + 0.34 \times 10^{-6} (1000)^3 + I(1000)$$

or
$$I = 8.34$$

At $T = 298^\circ \text{K}$ (25°C)

$$\Delta F = -9944 + 0.415(298) \ln (298) - 0.00238(298)^2 + 0.34 \times 10^{-6} (298)^3 + 8.34(298)$$

or
$$\Delta F = -6967$$

Calculation of Free Energy Data. Free energy changes for the evaluation of constant I in Equation (9) cannot be calculated directly from simple thermochemical data. The details of the methods utilized in developing data of this type are discussed in the more complete books on chemical thermodynamics but are too involved for presentation here.

Four methods are available for calculating the free energy change in a chemical reaction.

1. From actual measurements of the conditions of equilibrium the free energy change can be calculated by the equations of the following sections.

2. Free energies may be calculated from Equation (4), Chapter XII, with values of entropy calculated by use of heat-capacity data at low temperatures approaching the absolute zero.

3. Measurements of electrical potentials in balanced galvanic cells permit calculation of the free energy changes of the reactions taking place in the cells.

4. The free energy change of a reaction may be obtained from free energy changes in other reactions involving its products and reactants by combination of free energy equations in the same manner as heat of reaction equations were combined in Chapter VI.

Standard Free Energy Changes. When a reaction takes place under such conditions that each of the products and reactants is in its standard state of unit activity the accompanying free energy change is termed the *standard free energy change*. Since the definition of the standard state

fixes the pressures and states of the components the standard free energy change is affected only by temperature.

Free energy data are generally reported as standard molal free energies of formation when elements and compounds are in their standard states of unit activity.

In Table XXI are standard free energies of formation selected from various sources and expressed in calories per gram-mol. Many other data are available in the literature. Frequently these values are given at only one temperature, usually 25° C. A complete equation can be derived by the method of Illustration 1 if heat-capacity and heat-of-formation data are available.

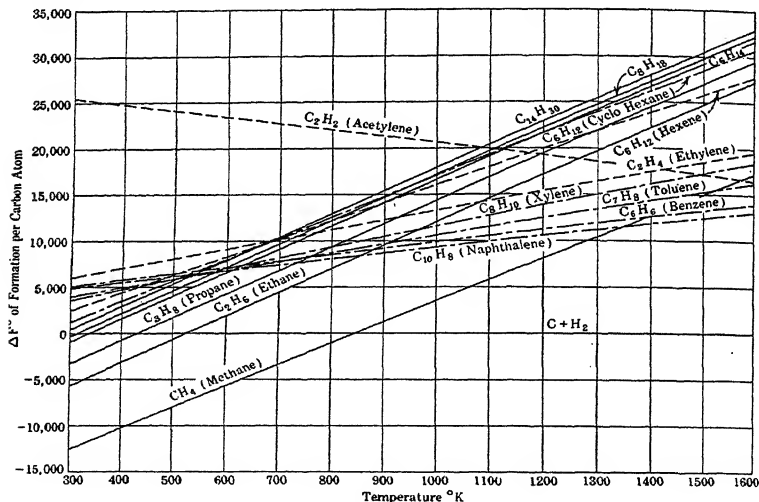


FIG. 91. Standard Free Energies of Formation of Hydrocarbons.*

* Taken from Parks and Huffman, "Free Energies of Some Organic Compounds," with permission of the Reinhold Publishing Corporation.

Additional data for the standard free energies of formation of hydrocarbons are shown in Fig. 91 from Parks and Huffman. In this figure the molal free energies of formation are expressed *per carbon atom* in order that the figure shall show visually the relative stabilities of the different compounds with respect to the elements. For example, the fact that the acetylene curve (C_2H_2) is positive indicates that over the entire temperature range this compound is thermodynamically unstable

and tends to decompose to carbon and hydrogen. Similarly, since the curve for propane (C_3H_8) is higher than that for ethane (C_2H_6) the latter compound is the more stable. Propane is unstable at temperatures above $450^\circ K$; ethane is stable up to $530^\circ K$.

The free energies of formation of the hydrocarbons are obtained by multiplying the values from Fig. 91 by the numbers of carbon atoms. The standard free energy changes of reactions involving these hydrocarbons may then be calculated by summations of the free energies of formation.

TABLE XXI

STANDARD FREE ENERGIES OF FORMATION AND REACTION
calories per gram-mol

From International Critical Tables, Vol. VII, 1930, unless otherwise noted.

Carbon Compounds (based on graphitic carbon)

For Hydrocarbons, see Fig. 91.

Carbon monoxide, $CO(g)$

$$\Delta F^\circ_F = -26,600 - 2.15 T \ln T + 2.15 \times 10^{-3} T^2 - 0.2 \times 10^{-6} T^3 - 8.20 T$$

Carbon dioxide, $CO_2(g)$

$$\Delta F^\circ_F = -94,110 + 0.60 T \ln T - 0.65 \times 10^{-3} T^2 + 0.11 \times 10^{-6} T^3 - 3.74 T$$

Methyl alcohol, $CH_3OH(g)^*$

$$\Delta F^\circ_F = -44,760 + 15.35 T \ln T - 12.0 \times 10^{-3} T^2 - 64.2 T$$

Ethyl alcohol, $C_2H_5OH(g)^*$

$$\Delta F^\circ_F = -49,770 + 20.45 T \ln T - 13 \times 10^{-3} T^2 - 75.5 T$$

Formaldehyde, $HCHO(g)^*$

$$\Delta F^\circ_F = -26,900 + 4.85 T \ln T - 0.005 T^2 - 23.5 T$$

Acetaldehyde, $CH_3CHO(g)^*$

$$\Delta F^\circ_F = -43,400 + 37.1 T$$

Acetic acid, $CH_3COOH(g)^*$

$$\Delta F^\circ_F = -105,300 + 47.1 T$$

Calcium Compounds

$CaCO_3(s) = CaO + CO_2(g)$

$$\Delta F^\circ = 42,216 - 2.4 T \ln T + 3.55 \times 10^{-3} T^2 + 0.31 \times 10^{-6} T^3 - 23.698 T$$

Halogen Compounds

Hydrogen iodide $HI(g)$

$$\Delta F^\circ_F = -1.270 + 0.45 T \ln T - 0.025 \times 10^{-3} T^2 - 5.01 T$$

Hydrogen bromide $HBr(g)$

$$\Delta F^\circ_F = -11,970 + 0.45 T \ln T - 0.025 \times 10^{-3} T^2 - 5.74 T$$

Hydrogen chloride $HCl(g)$

$$\Delta F^\circ_F = -21,870 + 0.45 T \ln T - 0.025 \times 10^{-3} T^2 - 5.31 T$$

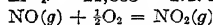
* Parks and Huffman "Free Energies of Some Organic Compounds," Chemical Catalog Co. (1933).

*Hydrogen Compounds*Water $\text{H}_2\text{O}(g)$

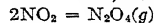
$$\Delta F^\circ_F = -57,410 + 0.94T \ln T + 1.65 \times 10^{-3}T^2 - 0.37 \times 10^{-6}T^3 + 3.92T$$

*Nitrogen Compounds*Nitric oxide $\text{NO}(g)$

$$\Delta F^\circ_F = 21,605 - 2.47T$$



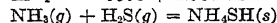
$$\Delta F^\circ = -14,170 + 2.75T \ln T - 2.8 \times 10^{-3}T^2 + 0.31 \times 10^{-6}T^3 + 2.73T$$



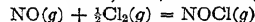
$$\Delta F^\circ = -13,600 + 41.6T$$

Ammonia $\text{NH}_3(g)$

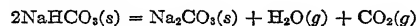
$$\Delta F^\circ_F = -9500 + 4.96T \ln T + 0.575 \times 10^{-3}T^2 - 0.85 \times 10^{-6}T^3 - 9.61T$$



$$\Delta F^\circ = -22,240 + 70.148T \text{ (from 277 to } 300^\circ \text{ K)}$$



$$\Delta F^\circ = -9100 + 14.3T$$

Sodium Bicarbonate

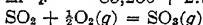
$$\Delta F^\circ = 30,600 - 81.86T$$

*Sulphur (based on gaseous sulphur)*Hydrogen sulphide, $\text{H}_2\text{S}(g)$

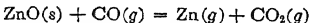
$$\Delta F^\circ_F = -19,200 + 0.94T \ln T + 1.65 \times 10^{-3}T^2 - 0.37 \times 10^{-6}T^3 + 1.65T$$

Sulphur dioxide, $\text{SO}_2(g)^*$

$$\Delta F^\circ_F = -83,260 + 2.75T \ln T - 2.8 \times 10^{-3}T^2 - 0.31 \times 10^{-6}T^3 + 0.90T$$

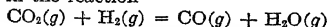


$$\Delta F^\circ = -22,600 + 21.36T$$

Zinc

$$\Delta F^\circ = +47,290 + 4.46T \ln T - 1.56 \times 10^{-3}T^2 - 0.2455 \times 10^{-6}T^3 - 60.305T$$

Illustration 2. Using the data of Table XXI, calculate the equation for the standard free energy change in the reaction



The free energy change of the reaction is obtained by subtracting the free energies of formation of the reactants from these of the products. This is equivalent to making a balance of the free energy of all components relative to their elements:

For the products, from Table XXI

$$\begin{aligned} \text{CO}(g), \Delta F^\circ_F &= -26,600 - 2.15T \ln T + 2.15 \times 10^{-3}T^2 - 0.2 \times 10^{-6}T^3 - 8.20T \\ \text{H}_2\text{O}(g), \Delta F^\circ_F &= -57,410 + 0.94T \ln T + 1.65 \times 10^{-3}T^2 - 0.37 \times 10^{-6}T^3 + 3.92T \end{aligned}$$

$$\text{Adding} \quad -84,010 - 1.21T \ln T + 3.80 \times 10^{-3}T^2 - 0.57 \times 10^{-6}T^3 - 4.28T$$

For the reactants,



$$\text{CO}_2(g), \Delta F^\circ_F = -94,100 + 0.60T \ln T - 0.65 \times 10^{-3}T^2 + 0.11 \times 10^{-6}T^3 - 3.74T$$

$$\text{Subtracting, } \Delta F^\circ = +10,090 - 1.81T \ln T + 0.00445T^2 - 0.68 \times 10^{-6}T^3 - 0.54T$$

From this equation the standard free energy change of the reaction may be calculated at any desired temperature.

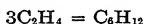
* Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co. (1923).

It will be noted that the equations derived for the water gas reaction in Illustrations 1 and 2 are considerably different. The standard free energy changes calculated from them at low temperatures differ widely, but in the higher temperature range where the reaction actually takes place at measurable rates and equilibrium studies have been made the results of the two equations agree fairly well.

These differences arise from the fact that the two equations are based on different heat-capacity equations, the differences of which are magnified when they are used for extension of free energy data over wide ranges of temperature. Unfortunate differences of this type exist throughout the data on free energies at present, and care must be taken that heat-capacity data be used consistently when dealing with free energy changes extended far from the temperatures of experimental data.

In this text the free energy data are for the most part taken from the International Critical Tables, Vol. VII, 1930, because of the extensive data presented and their general availability. However, the heat-capacity equations of Tables I to III differ considerably from those in the Critical Tables and are believed to be more reliable for general usage. For this reason great care must be exercised that consistent use is made of free energy and heat-capacity data when deriving equations in the manner of Illustration 1.

Illustration 3. Calculate the standard free energy change of the following reaction at 1000° K from the data of Fig. 91



For C_6H_{12} , ΔF_F° at 1000° K = $6 \times 16,000$

For C_2H_4 , ΔF_F° at 1000° K = $2 \times 13,600$

For the reaction $\Delta F^\circ_{1000^\circ \text{K}} = 6 \times 16,000 - 3 \times 2 \times 13,600 = 14,400$ cal per gram-mol.

The positive sign of the free energy change indicates that at this temperature the reaction would tend to reverse, cracking hexylene into ethylene rather than polymerizing the latter.

Free Energy Change in Change of Phase. The equilibrium vaporization of a liquid or the fusion of a solid under constant pressure are reversible processes in which the heat absorbed, q , is equal to both ΔH and $T\Delta S$, and the free energy change is zero. However, this is true only at equilibrium conditions. For example, water at 15° C has a vapor pressure of 12.5 millimeters of mercury. Vaporization of water at this temperature and pressure is accompanied by no free energy change. However, vaporization to form vapor at other than the equilibrium conditions is accompanied by a change in free energy as shown by the following equation at 15° C:



Here the free energy change is that accompanying the change in pressure of the vapor from 12.5 to 760 millimeters of mercury. Since at these low pressures the fugacities are approximately equal to the pressures, from Equation (2), Chapter XIII,

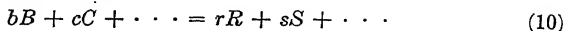
$$\Delta F_{298} = RT \ln \frac{760}{12.5} = (1.988) (298) (4.1) = 2430 \text{ cal per gram-mol}$$

Similarly in fusion or transitions in the solid state the free energy change is zero at equilibrium conditions. At other temperatures the free energy change may be either positive or negative and can be calculated from the heat capacity and heat of fusion or transition data by means of Equation (7).

By these methods it is possible to revise free energy data readily to apply to different phases. For example, in Table XXI the free energy of formation of gaseous water is given. From the above calculation the standard free energy of formation of liquid water at 15° C is less by 2430 calories per gram-mol. From the vapor-pressure data this correction could be determined at other temperatures and a complete equation established for the standard free energy of formation of liquid water. Since the standard state of liquids is atmospheric pressure, at high temperatures where pressures are large these calculations should include the free energy change accompanying change of pressure on the liquid calculated from Equation (22), Chapter XII.

THE EQUILIBRIUM CONSTANT

For developing the equations of chemical equilibrium the following general reaction will be considered:



where b , c , r , s are the number of mols of reactants and products B , C , R , and S , respectively.

When this reaction proceeds isothermally at any temperature T , starting with reactants at standard activities of unity and ending with products at unit activities, the accompanying standard change in free energy will be represented by the symbol ΔF° . The activity a_B° , a_C° , a_R° , a_S° of each component is unity.

If this same reaction proceeds isothermally until equilibrium conditions are established all the activities will adjust themselves to new values at which the change in free energy will be zero, or $\Delta F = 0$. At equilibrium the activities of the separate components will be represented by symbols, a_B , a_C , a_R , and a_S .

Setting up free energy balances of the reaction in the standard and the equilibrium states

$$\Delta F^\circ = rF_R^\circ + sF_S^\circ + \dots - bF_B^\circ - cF_C^\circ - \dots \quad (11)$$

$$\Delta F = rF_R + sF_S + \dots - bF_B - cF_C - \dots \quad (12)$$

where F = molal free energy. Combining (11) and (12)

$$\Delta F - \Delta F^\circ = r(F_R - F_R^\circ) + s(F_S - F_S^\circ) + \dots - b(F_B - F_B^\circ) - c(F_C - F_C^\circ) \quad (13)$$

Combining (2) and (13)

$$\Delta F - \Delta F^\circ = rRT \ln a_R + sRT \ln a_S + \dots -$$

or

$$\Delta F - \Delta F^\circ = RT \ln \frac{a_R^r a_S^s \dots}{a_B^b a_C^c \dots} \quad (14)$$

Since at equilibrium $\Delta F = 0$

$$-\Delta F^\circ = RT \ln \frac{a_R^r a_S^s \dots}{a_B^b a_C^c \dots} = RT \ln K \quad (15)$$

where K is the *equilibrium constant* at the temperature corresponding to the temperature of ΔF° .

$$K = \frac{a_R^r a_S^s \dots}{a_B^b a_C^c \dots} \quad (16)$$

From the relationship expressed by Equation (15) between the equilibrium constant and the standard free energy change ΔF° it is evident that K is a function only of temperature and is independent of pressure since the pressures of the standard states of all the components are constant.

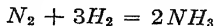
Where gases are involved in a reaction the definition of the standard state and therefore the numerical values of the standard free energy change and the equilibrium constant are dependent upon the units in which fugacities are expressed.

In order to avoid confusion in the expression of equilibrium constants and activities of gases it has become general practice always to express activities on the basis of fugacities in atmospheres. Then the standard state is at a fugacity of 1.0 atmosphere for all gases. All equilibrium constants here presented are on this basis.

In Fig. 92 are values of equilibrium constants derived from the data of Table XXI for representative reactions.

The numerical magnitude of K is also dependent upon the equation

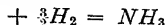
assigned to represent the number of reacting mols. For example, if the reaction for the synthesis of ammonia were designated as



the corresponding equilibrium constant would become

$$K' = \frac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3}$$

The same reaction may be written



Then,

$$K =$$

It is evident that, in this case, $K' = K^2$. It is hence always necessary to specify the number of mols assigned to the reaction.

EQUILIBRIUM CALCULATIONS

From Equation (15) conditions of partial pressures, concentrations, or composition of gases and solutions at equilibrium can be calculated. A knowledge of the standard free energy change is required as well as the relation of activities to molecular concentrations or partial pressures. These relationships have already been discussed. In summary, for ideal gases or gaseous mixtures, $a = p_B$; for actual gases where the fugacity rule applies, $a = N_B \gamma_B p$; for pure solids and liquids at atmospheric pressure $a = 1$; for solvents in perfect solutions $a_1 = N_1$; for solutes in perfect solutions or at infinite dilution $a_2 = N_2$. For more complex solutions and electrolytes the relations must be sought in more extensive treatises on chemical thermodynamics.

Gaseous Systems. Where all components involved are gases and the fugacity rule applies, substituting (5) in (16)

$$K = \left(\frac{1}{N_B^b N_C^c \dots} \right)$$

where

N_R = mol fraction of component R in the equilibrium mixture

γ_R = activity coefficient of R at the total pressure and temperature of the equilibrium

In a system containing n_I mols of inert gases not entering into the reaction,

$$N_R = \frac{n_R}{n_B + n_C + \dots + n_R + n_S + \dots + n_I} \quad (18)$$

where n_R = mols of R in the equilibrium mixture.

The ratio of the activity coefficients in Equation (17) is constant for a given temperature and pressure and is designated by K_γ .

$$\frac{\dots}{\dots} \quad (19)$$

However, unlike the equilibrium constant K , the term K_γ is affected by change in pressure as well as temperature.

For reactions at low pressures, in the neighborhood of atmospheric or below, the activity coefficients may be taken as unity and the term K_γ neglected. At higher pressures this term may have a marked effect on the equilibrium calculations and may be determined from Fig. 87, Chapter XIII.

Combining (17), (18), and (19)

(20)

Equation (20) is the most useful form of the equilibrium equation from which, if the equilibrium constant K is known, the composition of a reacting system at equilibrium may be directly calculated. This calculation is best carried out by expressing the number of mols of each active material present at equilibrium in terms of the equilibrium degree of completion, x , and the numbers of mols of components in the original unreacted mixture. These values are substituted in Equation (20) which is then solved for the equilibrium degree of completion, x . If the final equation to be solved is of a complicated form the graphical method described in Chapter XI, page 390, may be used.

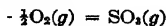
Illustration 4. The gases from the pyrites burner of a contact sulphuric acid plant have the following composition by volume:

SO ₂	7.8%
O ₂	10.8%
N ₂	81.4%
	<hr/> 100.0%

This gaseous mixture is passed into a converter where, in the presence of a catalyst, the SO₂ is oxidized to SO₃. The temperature in the converter is maintained at 500° C and the pressure at 760 mm of Hg. Calculate the composition of the gases leaving the converter, assuming that equilibrium conditions are reached. It may be assumed that the activity coefficients and K_γ are equal to unity.

Solution:

Basis: 100 lb-mols of the original mixture.



From Fig. 92, at 500° C (773° K) $\log K = 1.75$ or $K = 56$.

$p = 1.0$ atmosphere

Limiting reactant = SO_2

Let x = equilibrium degree of completion.

Composition of equilibrium mixture.

$$\text{SO}_2 = 7.8 - 7.8x \text{ lb-mols} = \dots\dots\dots n_{\text{SO}_2}$$

$$\text{SO}_3 = 7.8x = \dots\dots\dots n_{\text{SO}_3}$$

$$\text{O}_2 = 10.8 - 7.8 \frac{x}{2} \text{ lb-mols} = \dots\dots\dots n_{\text{O}_2}$$

$$\text{N}_2 = 81.4 \text{ lb-mols} = \dots\dots\dots n_{\text{N}_2}$$

From Equations (18) and (20):

$$\left[\frac{p}{(7.8 - 7.8x)(10.8 - 3.9x)^{\frac{1}{2}}(7.8x + 7.8 - 7.8x + 10.8 - 3.9x + 81.4)} \right]^{-1} = K$$

Substituting in this equation:

$$\left[\frac{7.8x}{(7.8 - 7.8x)(10.8 - 3.9x)^{\frac{1}{2}}} \right] \left[\frac{p}{7.8x + 7.8 - 7.8x + 10.8 - 3.9x + 81.4} \right]^{-1} = K$$

or

$$\left[\frac{7.8x}{(7.8 - 7.8x)(10.8 - 3.9x)^{\frac{1}{2}}} \right] \left[\frac{p}{100 - 3.9x} \right]^{-1} = K \quad (b)$$

Since $p = 1.0$ and $K = 56$, for graphical solution:

$$\frac{7.8x(100 - 3.9x)^{\frac{1}{2}}}{(7.8 - 7.8x)(10.8 - 3.9x)^{\frac{1}{2}}} - 56 = \Delta$$

The solution is obtained by assuming a series of values of x and calculating the corresponding values of Δ . These results are plotted, the value of x corresponding to $\Delta = 0$ being the correct solution. Using this method,

$$x = 0.94 \text{ or } 94\%$$

Composition of gases leaving the converter:

$\text{SO}_2 = 7.8 - (7.8 \times 0.94) = \dots\dots\dots$	0.47 lb-mol	0.5%
$\text{SO}_3 = 7.8 \times 0.94 = \dots\dots\dots$	7.33 lb-mols	7.6%
$\text{O}_2 = 10.8 - (3.9 \times 0.94) = \dots\dots\dots$	7.13 lb-mols	7.4%
$\text{N}_2 = \dots\dots\dots$	81.4 lb-mols	84.5%
Total = $\dots\dots\dots$	96.33 lb-mols	100.0%

This same procedure may be followed to calculate the degree of completion in any system at any conditions for which the necessary data are available. By repeating the calculations of Illustration 4 to correspond to other conditions of temperature and pressure, the effects of varying these conditions may be quantitatively predicted.

Under conditions of high pressure the activity coefficients cannot be neglected but the general method of solution is the same. Values of K , may be calculated directly from activity coefficients of the individual

components obtained from Fig. 87. Where a number of calculations are to be made for a particular system of reactants and products a chart may be prepared relating K_γ to temperature and total pressure. Fig. 93 is such a chart for the ammonia synthesis system where

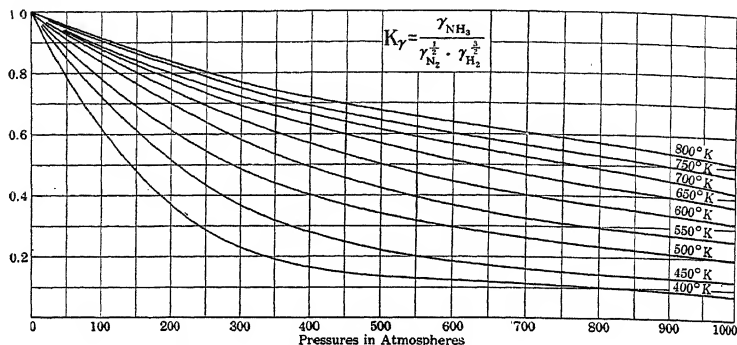


FIG. 93. Ratio of Activity Coefficients for Ammonia Synthesis.

Illustration 5. Calculate the equilibrium percentage conversion of nitrogen to ammonia at 700° K and a pressure of 300 atmospheres with the gas entering the converter having a composition of 75 mol per cent H_2 and 25 mol per cent N_2 .



At 300 atmospheres, 700° Kelvin, $K = 0.0098$ (Table XXI), and $K_\gamma = 0.72$ (Fig. 93).

Let x represent the number of mols of ammonia formed at equilibrium starting with $\frac{1}{2}$ mol N_2 and $\frac{3}{2}$ mols H_2 . Then

$$\frac{0.77x}{(1 - x)}$$

and $2 - x =$ total number of mols at equilibrium.

Substituting the above values in Equation (20),

or

$$x = 0.60$$

The percentage conversion of N_2 to NH_3 is hence 60 per cent, and the composition of the equilibrium mixture in mol per cent is

$$\begin{aligned} N_2 &= 14.3\% \\ H_2 &= 42.9\% \\ NH_3 &= 42.9\% \end{aligned}$$

Heterogeneous Reactions. Systems in which only one phase is present, such as gaseous systems, are said to be *homogeneous*. Systems in which more than one phase is visibly present are *heterogeneous*. Such systems include all mechanical mixtures of solids and suspension of solids or liquids in liquids or in gases.

Equation (15) is rigorously correct and may be applied to any system, whether homogeneous or heterogeneous. The only requirement is that the standard free energy change, ΔF° , shall correspond to the free energy change of the reaction with each reactant and product in the state of unit activity. Thus, the value of ΔF° is determined by the arbitrary definition of the standard states.

When a pure solid or a pure liquid is involved in a heterogeneous reaction its activity by the conventions of page 440 is unity if the pressure is 1.0 atmosphere. At higher pressures the activity is increased according to Equation (6). This effect is negligible at moderate pressures of a few atmospheres or less.

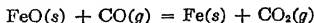
If in the reaction represented by Equations (10) and (17) there are, in addition to gaseous compounds B , C , R , and S , a solid or liquid reactant D and a solid or liquid product T , Equation (17) becomes

$$K = \frac{a_T}{a_D a_B a_C a_R a_S} \quad (21)$$

As pointed out above, the activities of the solids or liquids may be taken as unity at moderate pressures. In no case does the quantity present of the solid or liquid reactant affect the composition of the gaseous phase at equilibrium unless solutions are formed.

Illustration 6. Ferrous oxide, FeO , is reduced to metallic iron by passing a mixture of 20% CO and 80% N_2 over it at a temperature of 1000°C under a pressure of 1.0 atmosphere. Assuming that equilibrium conditions are reached in the process, calculate the weight of metallic iron produced per 1000 cu ft of gas introduced, measured at the conditions of the process. Activity coefficients may be assumed equal to 1.0.

The reaction taking place is as follows:



The equilibrium data of this reaction have not been completely evaluated, but at 1000°C it has been found that the equilibrium constant, K , corresponding to the above equation, is 0.403.

Basis: 1.0 lb-mol of entering gas.

Since the activities of the FeO and Fe equal 1.0 Equation (21) may be arranged in the form of (20). Then

$$n_{\text{CO}} \left[n_{\text{CO}} + n_{\text{CO}_2} \cdot \frac{1}{n_{\text{N}_2}} \right]^{1-1} = K$$

Basis: 100 lb-mols of the original mixture.

Let x = equilibrium degree of completion.

From Equation (b) of Illustration 4:

$$K = \frac{7.8x}{(7.8 - 7.8x)(10.8 - 3.9x)^{\frac{1}{2}}} \left(\frac{100 - 3.9x}{p} \right)^{\frac{1}{2}}$$

A series of values of x are selected and the corresponding values of K calculated, first with p equal to 1.0 and then 2.0 atmospheres. The corresponding temperatures, $T^{\circ}\text{K}$, are then obtained from Fig. 92. The calculations are tabulated as follows. In the column headings the numbers in parentheses represent the results contained in the columns bearing these numbers.

1	2	3	4	5	6	7	8
x	$7.8x$	$7.8 - 7.8x$	$3.9x$	$10.8 - 3.9x$	(5) [†]	(2) (3) × (6)	$100 - 3.9x$
0.50	3.9	3.9	1.95	8.85	2.98	0.336	98.0
0.70	5.45	2.35	2.73	8.07	2.84	0.816	97.3
0.90	7.02	0.78	3.51	7.29	2.70	3.34	96.5
0.95	7.41	0.39	3.70	7.10	2.66	7.15	96.3
0.98	7.64	0.16	3.82	6.98	2.64	18.0	96.2

x	$p = 1.0$				$p = 2.0$			
	9	10	11	12	13	14	15	16
	$\left[\frac{(8)}{p}\right]^{\frac{1}{2}}$	K	$\log K$	$T^{\circ}\text{K}$	$\left[\frac{(8)}{p}\right]^{\frac{1}{2}}$	K	$\log K$	$T^{\circ}\text{K}$
0.50	9.91	3.33	0.523	948	7.00	2.35	0.372	980
0.70	9.86	8.05	0.906	882	6.94	5.66	0.753	910
0.90	9.84	32.8	1.516	800	6.94	23.2	1.366	820
0.95	9.83	70.2	1.847	760	6.93	49.5	1.695	777
0.98	9.82	177	2.247	710	6.93	125	2.097	728

These calculations may be continued to correspond to other pressures. The results are plotted in curves E of Fig. 94, relating the equilibrium degree of completion, as ordinates, to temperature in degrees Centigrade. This chart is applicable only to systems of the particular initial composition here considered. Change in relative proportions of any of the original reactants renders the chart entirely inapplicable.

A chart of the type of curves E of Fig. 94 may be prepared for any reacting system and from it equilibrium degrees of completion may be readily estimated by interpolation. For example; at a temperature of 600°C and a pressure of 1.5 atmospheres it would be estimated from the E curves of Fig. 94 that the equilibrium degree of completion, of this particular reaction with this particular initial composition, will be about

76 per cent. If the initial composition of the reacting system undergoes change a new chart must be prepared to correspond to each different composition.

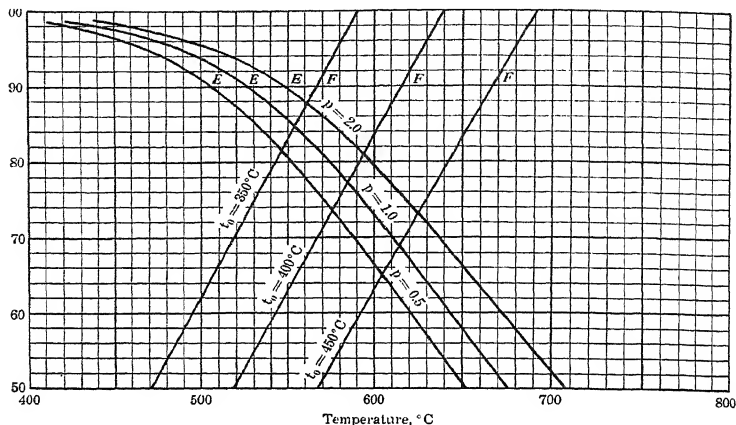


FIG. 94. Equilibrium Degree of Completion and Temperature Chart for Oxidation of SO_2 . Initial System, 7.8% SO_2 , 10.8% O_2 , 81.4% N_2 .

EFFECT OF REACTION CONDITIONS ON EQUILIBRIUM DEGREE OF COMPLETION

Equation (20) may be rearranged:

$$K = \frac{I}{J}^{r+s+t} \quad (22)$$

From inspection of this equation it is possible to predict the effects on the equilibrium degree of completion which are produced by changes in the conditions of the reaction. Any change which will increase the right-hand side of Equation (22) will tend to increase the ratio of products to reactants in the equilibrium mixture and correspond to an increased degree of completion.

Effect of Temperature. From Equation (22) it is apparent that an increased value of the equilibrium constant, K , must correspond to an increased degree of completion. The value of the equilibrium constant depends only upon temperature, as already discussed. It follows that the equilibrium degree of completion is increased by a rise in temperature

in the case of an endothermic reaction and decreased in the case of an exothermic reaction.

Effect of Pressure. It has been pointed out that the equilibrium constant, K , is independent of pressure. The value of K_γ is affected by pressure in a manner for which generalized predictions cannot be made. In addition, from inspection of Equation (22) it is apparent that the pressure under which a reaction proceeds will affect its equilibrium degree of completion in case the reaction produces a change in the total number of mols of gaseous components present in the system. If no change in the number of mols of gases is produced, the exponent $(r + s + \dots) - (a + b + \dots)$ will equal zero and the magnitude of the pressure p will have no effect on the extent of the reaction except as it affects K_γ .

However, *if a reaction produces a decrease in the total number of mols of gaseous components the equilibrium degree of completion will be increased by an increase in pressure.* If the total number of mols of gases is increased as a result of the reaction, an increase in pressure will diminish the equilibrium degree of completion. This is in accord with the Le Chatelier-Braun principle which was previously discussed.

Effect of Dilution with an Inert Gas. Dilution of a reacting system with an inert gas corresponds to an increase of n_I of Equation (22). The effect produced is similar to that of a decrease in pressure. Hence, *if a reaction produces an increase in the number of mols of gaseous components the equilibrium degree of completion will be increased by dilution with an inert gas.* If no change in the total number of mols of gases accompanies a reaction, the presence of inert gases will have no effect on the equilibrium degree of completion.

Effect of Excess Reactants. If component B of Equation (22) is the limiting reactant, increase in the number of mols of the other reactants, $C \dots$, will increase the number of mols of products, $R, S \dots$, and also the degree of completion of the reaction at equilibrium. Therefore, *the presence of excess of one reactant tends to increase the equilibrium degree of conversion of the other reactants present.*

Effect of Presence of Products in Initial Reacting System. It is apparent from Equation (22) that the presence, in the original unreacted system, of any of the compounds which are products of a reaction will diminish the amounts of these compounds which will be formed by the reaction in proceeding to equilibrium conditions. Therefore, *the addition of reaction products to the initial reacting system will diminish the equilibrium degree of completion of any reaction.*

EQUILIBRIUM REACTION TEMPERATURES

In Chapter VII methods were demonstrated whereby the temperature attained by a reacting system may be calculated if the reaction goes practically to completion without loss of heat from the system. In a reaction reaching equilibrium conditions which do not approach 100 per cent completion the temperature attained will depend on the degree of completion actually produced, which in turn depends on the temperature. The equilibrium temperature attained by such a reaction when proceeding adiabatically may best be determined by a graphical calculation, making use of the degree of completion chart of the system.

On a degree of completion chart of the type of curves *E* of Fig. 94, page 458, a curve is plotted relating calculated adiabatic reaction temperature to degree of completion. This curve may be established by selecting a series of values of degree of completion and calculating the reaction temperature corresponding to each by the method discussed in Chapter VII, page 229. The values on this curve are independent of pressure where it may be assumed that heat capacities are independent of pressure. However, an entirely new curve must be plotted to correspond to each change in the initial temperatures of any of the reactants.

The point of intersection between a curve relating degree of completion to calculated reaction temperature and a curve relating equilibrium degree of completion to temperature will represent the equilibrium temperature and degree of completion attained by the reaction under the conditions of initial temperature and pressure corresponding to the two curves. By constructing charts of such curves to correspond to a specific reacting system of *constant initial composition*, the equilibrium temperature and degree of completion corresponding to any selected operating conditions may be readily predicted.

In the following illustration this method of calculation is demonstrated by applying it to the system which was considered in Illustrations 4 and 7.

Illustration 8. The mixture of 7.8% SO₂, 10.8% O₂, and 81.4% N₂ discussed in Illustrations 4 and 7 enters the converter at a temperature of 400° C. Calculate the equilibrium temperature attained in the converter, assuming that it is thermally insulated so that heat loss is negligible.

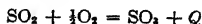
Solution:

Basis: 100 gram-mols of the original gaseous mixture.

Reference temperature: 0° C. Since the reaction temperatures are relatively high it is permissible to assume that the standard heat of reaction at 0° C is equal to that at 18° C.

α = degree of completion.

Standard Heat of Reaction at 0° C.



From the heat of formation data, Table X, page 159.

$$\begin{aligned} Q &= 91,500 - 69,400 = \dots\dots\dots 22,100 \text{ calories (gram-mols)} \\ \text{SO}_2 \text{ converted} &= \dots\dots\dots 7.8x \text{ gram-mols} \\ \text{Total standard heat of reaction} &= (7.8x) \\ (22,100) &= \dots\dots\dots 172,400x \text{ calories} \end{aligned}$$

Heat Content of Reactants.

Mean heat capacity between 0° and 400° C (from Fig. 12, page 116).

$$\begin{aligned} \text{SO}_2 &= 10.0 \times 7.8 = \dots\dots\dots 78 \text{ calories per } ^\circ\text{C} \\ \text{O}_2, \text{ N}_2 &= 7.1 \times 92.2 = \dots\dots\dots 655 \text{ calories per } ^\circ\text{C} \\ \text{Total} &= \dots\dots\dots 733 \text{ calories per } ^\circ\text{C} \end{aligned}$$

Heat content of reactants = $400 \times 733 = 293,000$ calories.

Heat Content of Products.

Let t° C = temperature of reaction.

Mean heat capacity between 0° C and t° C: The data for SO_2 , O_2 and N_2 may be derived from Table I, page 113. The mean molal heat capacity of SO_2 from 0 to t° C may be represented by $11.1 + 0.002t$ on the basis of the assumptions discussed in Illustration 7 of Chapter VII, page 226.

$$\begin{aligned} \text{SO}_2 &= (7.8 - 7.8x) (9.085 + 0.0024t - 0.277 \times 10^{-6}t^2) \\ \text{O}_2, \text{ N}_2 &= (92.2 - 3.9x) (6.935 + 0.000338t + 0.43 \times 10^{-7}t^2) \\ \text{SO}_2 &= 7.8x(11.1 + 0.002t) \end{aligned}$$

Simplifying these equations:

$$\begin{aligned} \text{SO}_2 &= (70.9 + 0.0187t - 2.16 \times 10^{-6}t^2) + x(-70.9 - 0.0187t + 2.16 \times 10^{-6}t^2) \\ \text{O}_2, \text{ N}_2 &= (639 + 0.0312t + 3.97 \times 10^{-6}t^2) + x(-27.0 - 0.0013t - 0.17 \times 10^{-6}t^2) \\ \text{SO}_2 &= \dots\dots\dots + x(86.5 + 0.0156t) \\ \text{Total} &= (709.9 + 0.0499t + 1.8 \times 10^{-6}t^2) + x(-11.4 - 0.0044t + 1.99 \times 10^{-6}t^2) \end{aligned}$$

Total heat content of products =

$$(709.9t + 0.0499t^2 + 1.81 \times 10^{-6}t^3) + x(-11.4t - 0.0044t^2 + 1.99 \times 10^{-6}t^3)$$

Heat Balance. Equating the heat content of the products to the sum of the standard heat of reaction and the heat content of the reactants:

$$\begin{aligned} 172,400x + 293,000 &= (709.9t + 0.0499t^2 + 1.81 \times 10^{-6}t^3) + x(-11.4t \\ &\quad - 0.0044t^2 + 1.99 \times 10^{-6}t^3) \end{aligned}$$

Solving for x :

$$x = \frac{-293,000 + 709.9t + 0.0499t^2 + 1.81 \times 10^{-6}t^3}{172,400 + 11.4t + 0.0044t^2 - 1.99 \times 10^{-6}t^3}$$

This equation permits direct calculation of values of x corresponding to selected values of t .

	x
400	0.0
500	0.415
550	0.625
600	0.835
650	1.046

These values are plotted in the F curve of Fig. 94, page 458, corresponding to an initial temperature, t_0 , of 400°C . This curve crosses the E curve corresponding to a pressure of 1.0 atmosphere at the point corresponding to a temperature of 585°C and a degree of completion of 77%. These are the equilibrium conditions of the reaction.

The F curves of Fig. 94 relate calculated reaction temperatures to degrees of completion, each corresponding to a different initial temperature of the reactants entering the converter. These curves were established by the method demonstrated in Illustration 6. Such a chart may be constructed in a similar manner to apply to any system for which the necessary data are available. From Fig. 94 the equilibrium temperature and degree of completion corresponding to any selected adiabatic operating conditions may be readily estimated. For example, if the reacting gases enter the converter at a temperature of 375°C and a pressure of 1.5 atmospheres, an equilibrium temperature of 575°C and a degree of completion of 83 per cent will be attained.

If a reaction cannot be assumed to proceed under adiabatic conditions a chart of the type of Fig. 94 can be constructed which takes into account the loss of heat from the reacting system. Such losses in no way affect the E curves. However, the heat losses, expressed as a function of the temperature of the system, must be included in the heat balance equation from which the data for the F curves are calculated.

Equilibrium Reaction Temperatures at High Pressures. When reactions proceed at high pressures the method described for obtaining the equilibrium reaction temperature should be modified to take into consideration the effect of pressure upon heat contents, heat capacities, and activities of the component gases. For example, if a 1 : 3 mixture of nitrogen and hydrogen enters a catalytic reaction chamber at 400°C and reacts adiabatically to equilibrium at 300 atmospheres the temperature leaving will be 590°C with a corresponding percentage conversion of nitrogen to ammonia of 25 per cent. If the results were calculated neglecting the effect of pressure upon heat capacities and activities the calculated results would be 600°C with a corresponding conversion of 21 per cent. The smaller temperature rise under actual conditions is due to the increased heat capacity of ammonia at 300 atmospheres, and the increased percentage conversion is due to the decrease in activity of ammonia as compared to nitrogen and hydrogen.

EFFECT OF CATALYSTS AND RADIANT ACTIVATION ON THE EQUILIBRIUM CONDITIONS

Catalysts are found to have no effect on the equilibrium conditions reached in gaseous reactions at low pressures. From this fact it must be concluded that a catalyst has no effect upon the activities of the

components present. However, the rate at which a reacting system attains equilibrium will be greatly hastened by the presence of a catalyst even though the final equilibrium conditions are the same as though the catalyst were absent.

The absorption of radiant energy from an external source may greatly affect the activities of components in a reacting system. Where reactions are involved which are photochemical in nature, that is, strongly influenced by radiant energy, the effects of the intensity and types of radiation present are of great importance and must be carefully considered in attempting to predict equilibrium conditions.

All the equilibrium data presented in this chapter correspond to reactions taking place in the absence of radiation from external sources. This limitation applies to the majority of the equilibrium data of the literature. When a substance at a given temperature and pressure absorbs radiant energy there is an accompanying free energy change and an increase in fugacity and activity. In a reacting system these changes in activity produce changes in equilibrium composition.

For example, in the oxidation of SO_2 to SO_3 at a temperature of 45°C the reaction theoretically proceeds to an equilibrium composition corresponding to practically 100 per cent completion, or a product of pure SO_3 , if conducted in the dark. However, it has been found that at this same temperature under the influence of a strong ultraviolet light the equilibrium is shifted, corresponding to a mixture containing only 60 per cent SO_3 if the original reactants were in combining proportions.

EQUILIBRIA IN COMPLEX SYSTEMS

In many industrial processes several concurrent or successive reactions take place simultaneously. When complete equilibrium conditions are established in such a complex system the concentrations of all the components must adjust themselves to such values that the equilibrium equation of every possible reaction is satisfied. For example, in the oxidation of carbon the following reactions occur:

- (1) $\text{C}(s) + \text{O}_2(g) = \text{CO}_2(g)$
- (2) $\text{C}(s) + \frac{1}{2}\text{O}_2(g) = \text{CO}(g)$
- (3) $\text{C}(s) + \text{CO}_2(g) = 2\text{CO}(g)$
- (4) $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) = \text{CO}_2(g)$

When equilibrium is established between carbon and oxygen the concentrations of CO , CO_2 , and O_2 must be such that the equilibrium equation of each of these reactions is satisfied.

The equilibrium composition in a complex reacting system may be calculated algebraically by assigning a different symbol, x , y , or z , etc., to

represent the equilibrium degree of completion of each possible reaction. The equilibrium composition is then expressed in terms of these symbols and the equilibrium equation of each reaction written. In this way a series of equations is obtained which may be solved simultaneously for the unknown equilibrium degrees of completion.

Complete equilibrium calculations in complex systems become very tedious and simplifying assumptions are frequently desirable. In general it is permissible to neglect the equilibrium of any reaction whose equilibrium constant is either very large or very small in comparison to those of other reactions taking place in the system. If the equilibrium constant is very large it may be considered that the reaction goes to completion, or if the constant is very small it may be assumed that the reaction does not proceed.

For example, in the oxidation of carbon, mentioned above, the equilibrium constants at 1000° C of reactions (1), (2), and (4) are very large in comparison to that of reaction (3). In combustion calculations it is ordinarily sufficient to neglect the equilibria of these three reactions, assuming that they go to completion and that no oxygen is present in the system at equilibrium. The relative proportions of CO and CO₂ in the equilibrium system may then be calculated by consideration of only reaction (3).

ACTUAL DEGREES OF COMPLETION

The methods of calculating the final compositions of reacting systems which are considered in this chapter apply only when equilibrium conditions are reached. However, industrial reactions are usually not given opportunity to proceed to equilibrium and the value of these calculations is hence limited. Equilibrium conditions represent the goal toward which a chemical reaction is directed and beyond which it cannot proceed. Equilibrium calculations are of value only in determining this goal and tell nothing about the actual extent to which a reaction will proceed in a given period of time under specified conditions. It must be clearly understood that these calculations are applicable only to the limiting conditions of equilibrium.

The actual extent to which a chemical reaction will proceed depends on the net rate of change which is produced and upon the time allowed as well as upon the limiting equilibrium composition. Any means of increasing the net rate at which the composition of a reacting system changes toward equilibrium conditions will tend to increase the actual degree of completion obtained in any specified time interval which is insufficient for the attainment of equilibrium. Also, any means of increasing the degree of completion corresponding to equilibrium will

tend to increase the actual degree of completion obtained in any process.

As previously pointed out, the velocity at which a reaction proceeds, or the net rate of change in a reacting system, may be increased by the following changes:

- a. Increase in temperature.
- b. Increase in pressure.
- c. Provision of a positive catalyst.
- d. Activation by radiation.
- e. Agitation of the reacting system.

Any of these changes will increase the rate at which a reacting system will approach equilibrium and will tend to increase the actual degree of completion attained in a given time.

As previously discussed, the equilibrium degree of completion of a reaction may be varied by changes in temperature or pressure, by the introduction of an inert gas, or by means of photochemical activation. The direction of the change produced in the equilibrium degree of completion by variation of these factors is dependent on the nature of the reaction. Thus, it is possible for a change in operating conditions to have two opposing effects in determining the actual degree of completion obtained in a given time when equilibrium is not reached. For example, an increase in temperature will always increase the rate of approach to equilibrium but in the case of an exothermic reaction it will diminish the degree of completion at equilibrium. In such a case the net effect of the change on the actual degree of completion cannot be predicted without quantitative data on reaction rates, and there will be some optimum temperature of operation which will yield the highest degree of completion in a given time. However, if a change increases both the reaction rate and the equilibrium degree of completion its effect will always be to increase the actual degree of completion. For example, increasing the temperature of an endothermic reaction will increase both the rate of reaction and the equilibrium degree of completion and will always produce an increase in the actual degree of completion.

Another indeterminate factor in operation is the effect of pressure upon a gaseous reaction which proceeds with an increase in number of mols. An increase in pressure upon the system will increase the rate of reaction because of increased concentration but on the other hand will decrease the degree of completion at equilibrium. Operation at very low pressures will result in a greater equilibrium degree of completion, but it will also decrease the rate of reaction in the system and thereby decrease the capacity of the equipment. It will be desirable to select

an optimum pressure which will be determined by relative operating costs per unit weight of product and the cost of unconverted reactants which are wasted. Ordinarily gaseous reactions of this nature are conducted at atmospheric pressure since this pressure involves no additional expense in equipment.

A third indeterminate condition is the effect of dilution with an inert gas in a gaseous reaction or with solvent in a liquid reaction upon the actual degree of completion of a reaction which produces an increased number of mols of gaseous or dissolved materials. The effect of dilution will be to decrease the rate of reaction but to increase the equilibrium degree of completion.

The final selection of optimum operating conditions must always be based upon economic considerations. The operating conditions should be adjusted to produce an actual degree of completion which is so high that the saving resulting from further increase in the degree of completion will not pay for the additional cost of equipment and operation which is necessary to produce it. In general, the cost of equipment and operation increases rapidly as operating temperatures and pressures deviate increasingly from those of the atmosphere.

PROBLEMS

1. Nitrogen tetroxide dissociates into nitrogen peroxide according to the following reaction:



Calculate the equilibrium composition of the mixture formed from the dissociation of pure N_2O_4 under the following conditions:

- a. A temperature of 500°K and a pressure of 1.0 atmosphere, assuming $K_\gamma = 1$.
- b. A temperature of 1000°K and a pressure of 1.0 atmosphere, assuming $K_\gamma = 1.0$.

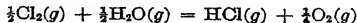
2. Carbon dioxide is reduced by graphite according to the equation:



Assuming that equilibrium is attained, calculate the degree of completion of the reduction of pure CO_2 under the following conditions:

- a. A temperature of 1000°K and a pressure of 1.0 atmosphere, assuming $K_\gamma = 1.0$.
- b. A temperature of 1400°K and a pressure of 1.0 atmosphere, assuming $K_\gamma = 1.0$.
- c. A temperature of 1000°K and a pressure of 100 atmospheres.

3. Water and chlorine react at elevated temperatures according to the following equation:

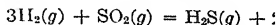


The critical data of the components are as follows:

	Critical Temp. °C	Critical Pressure, atm
Cl ₂	144	76
H ₂ O	374	218
HCl	51	82
O ₂	-119	50

- From the data of Table XXI derive an equation for the standard free energy change of this reaction.
- Calculate the composition of the equilibrium mixture at 500° C, starting with equal volumes of chlorine and water at atmospheric pressure (assume $K_v = 1.0$)
- Repeat the calculation of part *b* for a pressure of 100 atm.

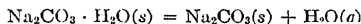
- Sulphur dioxide is reduced by hydrogen according to the following equation:



- From the data of Table XXI derive an equation for the standard free energy change of this reaction.
- Calculate the equilibrium composition of the mixture obtained at 1200° C and atmospheric pressure, starting with 3 parts of hydrogen and 1 part of SO₂.
- Repeat the calculation of part *b* at 100 atmospheres using the following critical data:

	Critical Temperature, °C	Critical Pressure, atm
H ₂ (see page 399)	-240	12.8
SO ₂	157	78
H ₂ S	100	89
H ₂ O	374	218

- The hydrate of sodium carbonate decomposes according to the following equation:



The equilibrium pressure in atmospheres of the water vapor in this reaction is given by the following equation:

$$\log p = 7.944 - 3000.0/T^\circ \text{K}$$

Derive an expression for the standard free energy change of this reaction.

- Potassium bicarbonate is decomposed according to the following equation:



The equilibrium pressure in atmospheres of the CO₂ and H₂O formed in this reaction is expressed by the following equation:

$$\log p = 7.951 - 3420/T^\circ \text{K}$$

Derive an equation for the standard free energy change of this reaction.

- Methyl alcohol is synthesized by passing a mixture of CO and H₂ over a catalyst according to the following equation:

Calculate the composition of the equilibrium mixture obtained at a temperature of 300° C and a pressure of 240 atmospheres starting with 2 parts of H₂ and 1 part of CO, assuming that only this reaction takes place. The critical temperature of CH₃OH is 240° C and the critical pressure 79 atmospheres.

8. Methyl alcohol is oxidized by air to formaldehyde at 550° C in a catalyst chamber at atmospheric pressure. Calculate the percentage yield of formaldehyde using the theoretical air supply and assuming no further oxidation.

9. A mixture of 79% N₂ and 21% CO₂ by volume is passed over hot carbon (graphite) at a temperature of 1000° K and a pressure of 1.0 atmosphere. Calculate the equilibrium composition of the gases and compare this result with that of part *a* of Problem 2.

10. Carbon monoxide is burned with pure oxygen in the theoretically required proportions. Calculate the degrees of completion of the oxidation if equilibrium is attained at temperatures of respectively 1000° K and 3000° K under a pressure of 1.0

11. Water gas leaves a generator containing 51.1% H₂, 2.3% CO₂, and 46.6% CO by volume on the dry basis. Ten per cent of the steam which was introduced into the bottom of the generator passed through the bed of hot coke without decomposition and is present in the gases. This gaseous mixture is passed into a reaction chamber under a pressure of 1.0 atmosphere in contact with a catalyst of chromium oxide and allowed to attain equilibrium at a temperature of 700° K (423° C). Calculate the equilibrium composition of the gaseous mixture.

12. One volume of the initial wet water gas described in Problem 11 is mixed with three volumes of additional water vapor. This mixture is passed into the reaction chamber operated at the conditions described in Problem 11 and allowed to reach equilibrium.

a. Calculate the equilibrium composition of the gaseous mixture.

b. Calculate the composition of the residual gas if the CO₂ and H₂O are removed from the gaseous mixture of part *a* after equilibrium is attained.

13. In the Birkeland-Eyde process the nitrogen of the atmosphere is oxidized in a long, flaming electric arc.



Assuming that only this reaction takes place, calculate the percentage conversion of nitrogen to NO in air of average atmospheric composition at a pressure of 1.0 atmosphere and at temperatures of respectively 2000° K and 4000° K.

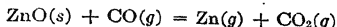
14. In the American process of synthesizing ammonia a mixture of three volumes of hydrogen and one volume of nitrogen is passed into a reaction chamber in contact with a catalyst of granular iron oxide combined with oxides of potassium and aluminum. Using the data of Illustration 5 and Fig. 93:

a. Plot curves relating the equilibrium degree of completion of this reaction to temperature at pressures of 1.0, 100, and 300 atmospheres. The temperature range from 400° K to 800° K should be included in the calculations.

b. Calculate the equilibrium degree of completion of the above reaction at a pressure of 200 atmospheres and a temperature of 750° K.

15. In the synthesis of ammonia described in Problem 14 the mixture of N_2 and H_2 is introduced into the reaction chamber under a pressure of 300 atmospheres and a temperature of $400^\circ C$. Assuming that heat loss from the reaction chamber is negligible, calculate the equilibrium reaction temperature, using the curves of Problem 14.

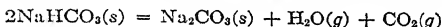
16. Zinc oxide is reduced with carbon monoxide under a pressure of 1.0 atmosphere according to the following reaction:



Calculate the degree of completion of the oxidation of CO at atmospheric pressure under the following different conditions, assuming that equilibrium conditions are attained and that ZnO is always present.

- At a temperature of $1000^\circ C$ using pure CO.
- At a temperature of $1500^\circ C$ using pure CO.
- At a temperature of $1000^\circ C$ using a mixture of 27.5% CO, 4.3% CO_2 , and 68.2% N_2 by volume.
- At a temperature of $1500^\circ C$ using a mixture of 27.5% CO, 4.3% CO_2 , and 68.2% N_2 by volume.

17. Sodium bicarbonate is calcined according to the following equation:



Calculate the pressure of the equimolecular mixture of H_2O and CO_2 in equilibrium with $NaHCO_3$ at a temperature of $100^\circ C$.

18. Limestone is calcined according to the following equation:



- Calculate the burning temperature necessary to evolve the CO_2 at a pressure of 1.0 atmosphere.
- What is the partial pressure of CO_2 at $1000^\circ C$?

19. Considering each of the following reactions:



Tabulate the effects of the following changes upon: (a) the velocity of reaction (mols transformed per unit time per unit volume); (b) the equilibrium degree of completion; (c) the actual degree of completion obtained in a specified time interval.

- Increase of temperature.
- Increase of pressure.
- Provision of a positive catalyst.
- Dilution with an inert gas.
- Agitation of the reacting system.

Tabulate each effect as an increase, decrease, no effect, or as indeterminate.

20. Acetylene gas and pure oxygen at $60^\circ F$ and 1 atmosphere pressure are supplied to an acetylene welding torch in the ratio of 1 volume of oxygen to 1 volume of acetylene. The primary reaction in the inner cone of the flame is $C_2H_2 + O_2 = 2CO$

The hydrogen in turn partly dissociates to monatomic hydrogen.

- a. Calculate the maximum temperature in degrees Fahrenheit of this inner cone and the corresponding equilibrium degree of dissociation of hydrogen to monatomic hydrogen assuming adiabatic conditions in the inner cone.
- b. What will be the temperature if the inner cone radiates 40,000 Btu per pound-mol of acetylene burned?

The equilibrium constant for the reaction $\text{H}_2 = 2\text{H}$ is as follows:

$$R \ln K_p = -\frac{97,000}{T} + 8.05 \log T - 0.00045T - 1.17$$

where T is in degrees Kelvin.

APPENDIX

THE I. C. T. ATOMIC WEIGHTS OF THE MORE COMMON ELEMENTS

	A				
Argon	Al	39.91	Manganese	Mn	54.93
Aluminum	Sb	26.96	Mercury	Hg	200.6
Antimony	As	121.77	Molybdenum	Mo	96.0
Arsenic	Ba	74.96	Neon	Ne	20.2
Barium	Bi	137.37	Nickel	Ni	58.68
Bismuth	B	209.0	Nitrogen	N	14.01
Boron	Br	10.82	Oxygen	O	16.00
Bromine	Cd	79.92	Phosphorus	P	31.02
Cadmium	Ca	112.41	Platinum	Pt	195.2
Calcium	C	40.07	Potassium	K	39.1
Carbon	Cl	12.00	Selenium	Se	79.2
Chlorine	Cr	35.46	Silicon	Si	28.06
Chromium	Co	52.01	Silver	Ag	107.88
Cobalt	Cu	58.97	Sodium	Na	23.0
Copper	F	63.57	Strontium	Sr	87.62
Fluorine	Au	19.00	Sulphur	S	32.06
Gold	H	197.2	Tellurium	Te	127.5
Hydrogen	He	1.008	Tin	Sn	118.70
Helium	I	4.00	Titanium	Ti	47.9
Iodine	Fe	126.93	Tungsten	W	184.0
Iron	Pb	55.84	Vanadium	V	50.96
Lead	Si	207.20	Zinc	Zn	65.38
Lithium	Mg	6.94	Zirconium	Zr	91.0
Magnesium		24.32			

FACTORS FOR CONVERSION OF ENERGY UNITS*

	Gram-calories	Btu	Joules	Foot-pounds	Kilogram-meters
Gram-calorie	1	3.968×10^{-3}	4.185	3.087	0.4267
Btu	252	1	1055	777.9	107.5
Joule	0.2389	9.482×10^{-4}	1	0.73756	0.1019
Foot-pound	0.3240	1.286×10^{-3}	1.356	1	0.13826
Kilogram-meter	2.343	9.298×10^{-3}	9.806	7.2327	1
Liter-atmos.	24.21	9.607×10^{-2}	101.32	74.733	10.333
Chu	453.6	1.8	1899	1400	193.5

	Liter-atmos.	Cu ft-atmos.	Foot-pounds	Horsepower hours
Gram-calorie	4.130×10^{-2}	1.459×10^{-2}	99.31	1.5591×10^{-6}
Btu	10.41	0.3676	25030	3.929×10^{-4}
Joule	9.689×10^{-3}	3.485×10^{-4}	23.73	3.725×10^{-7}
Foot-pound	1.3381×10^{-2}	4.7253×10^{-4}	32.174	5.0505×10^{-7}
Kilogram-meter	9.678×10^{-2}	3.4177×10^{-3}	232.7	3.6529×10^{-6}
Liter-atmos.	1	3.5319×10^{-2}	2403.8	3.7734×10^{-6}
1 Chu	13.74	0.6617	45054	7.072×10^{-4}

* From Perkins' "Introduction to General Thermodynamics," John Wiley & Sons, Inc., Publishers, with permission.

TABLE OF FACTORS AND CONSTANTS FOR CHEMICAL CALCULATIONS

Analysis of Air

By weight: oxygen, 23.2%; nitrogen, 76.8%	
By volume: oxygen, 21.0%; nitrogen, 79.0%	
Average molecular weight of air =	29
Average molecular weight of atmospheric nitrogen =	28.2

Capacity

1 gill =	4 fluid ounces
1 pint =	4 gills
1 quart =	2 pints
1 U. S. gallon =	4 quarts
1 U. S. gallon =	3.785 liters
1 U. S. gallon =	231 cubic inches
1 British gallon =	1.20094 U. S. gallons
1 cubic foot =	7.481 gallons
1 liter =	1.057 quarts
1 U. S. fluid ounce =	29.57 cubic centimeters

Physical Constants

The Gas Law Constant R

$R = 1.9885$ calories per gram-mol per degree Kelvin
$R = 82.06$ cubic centimeter-atmospheres per gram-mol per degree Kelvin
$R = 10.71$ pounds per square inch cubic feet per pound-mol per degree Rankine
$R = 0.729$ atmosphere cubic feet per pound-mol per degree Rankine

1 faraday = 96,500 coulombs

Avogadro constant = 6.06×10^{23} per gram-atom

Density

1 gram-mol of perfect gas at 0° C, 760 mm of mercury = 22.414 liters	
1 pound-mol of perfect gas at 0° C, 760 mm of mercury = 359.0 cubic feet	
Density of dry air at 0° C, 760 mm of mercury = 1.293 grams per liter or . . .	0.0807 pound per cubic foot
1 gram per cc =	62.4 pounds per cubic foot
1 gram per cc =	8.337 pounds per U. S. gallon

Length

1 inch =	2.540 centimeters
1 mile =	1.609 kilometers
1 mile =	5280 feet
1 micron =	10^{-6} meter
1 Angström unit =	10^{-10} meter

TABLE OF FACTORS AND CONSTANTS FOR CHEMICAL CALCULATIONS. — *Continued*

Mass

1 dram (avoirdupois) =	27.34 grains
1 ounce (avoirdupois) =	16 drams
1 pound =	16 ounces
1 pound =	7000 grains
1 pound =	453.6 grams
1 ton (short) =	2000 pounds
1 gram =	15.43 grains
1 kilogram =	2.205 pounds (avoirdupois)

Mathematical Constants

e =	2.7183
π =	3.1416
$\ln N$ =	$2.303 \log N$

Power

1 kilowatt =	56.92 British thermal units per minute
1 kilowatt =	1.341 horsepower
1 horsepower =	550 foot-pounds per second
1 watt =	44.24 foot-pounds per minute
1 watt =	14.34 calories per minute

Pressure

1 pound per square inch =	2.04 inches of mercury
1 pound per square inch =	2.31 feet of water
1 atmosphere =	14.7 pounds per square inch
1 atmosphere =	760 mm of mercury
1 atmosphere =	29.92 inches of mercury

Temperature Scales

Degrees F =	$1.8 (\text{degrees C}) + 32$
Degrees K =	$\text{degrees C} + 273.18$
Degrees R =	$\text{degrees F} + 459.7$

Volume

1 cubic inch =	16.39 cubic centimeters
1 liter =	61.02 cubic inches
1 cubic foot =	28.32 liters
1 cubic meter =	1.308 cubic yards
1 cubic meter =	1000 liters

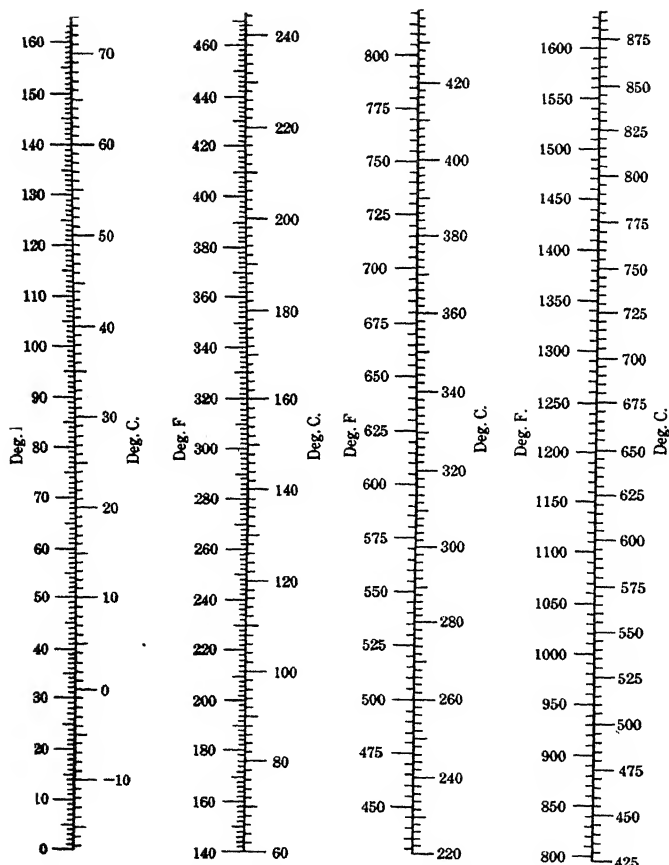


FIG. 95. Temperature Conversions.

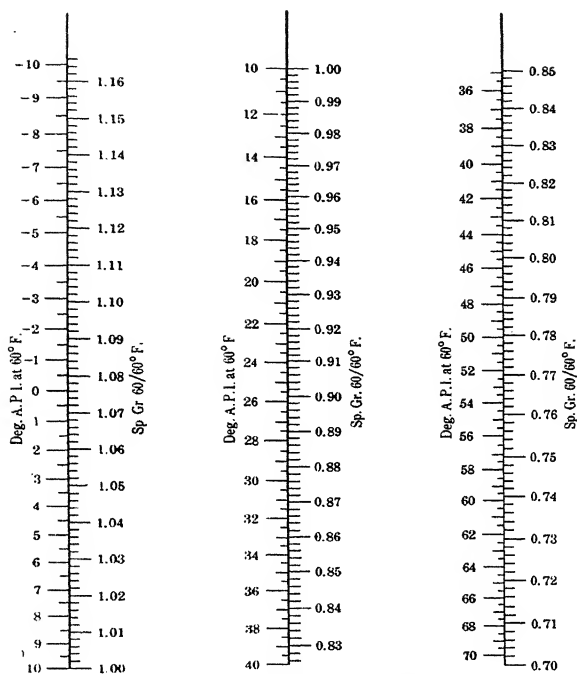


FIG. 96. Gravity Conversions.

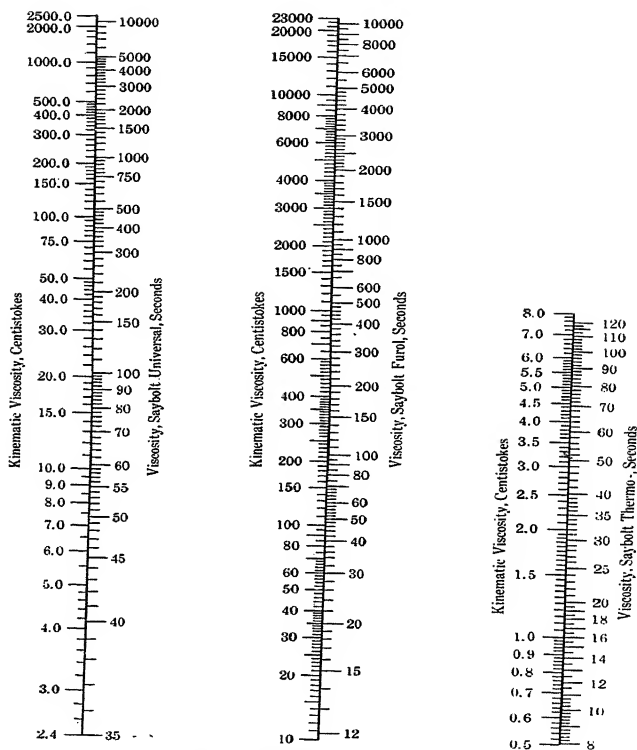


FIG. 97. Viscosity Conversions.

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